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Properties Enhancement of Wood by Cross-Linking Formation and Its Application to the Reconstituted Wood Products*¹

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Contents

Introduction

Chapter 1 Properties Enhancement of Solid Wood by Cross-Linking Formation

- 1.1 Biological Resistance of Formaldehyde-Treated Wood
- 1.2 Biological Resistance of Wood Treated with Non- or Low-Formaldehyde Reagents
- 1.3 Weathering Properties of the Wood Modified with Cross-Linking Reagents

Chapter 2 Application of Cross-Linking Formation to the Reconstituted Wood Products

- 2.1 Properties Enhancement of the Laminated Veneer Lumber (LVL) Modified with Some Cross-Linking Reagents
- 2.2 Dimensional Stability and Biological Resistance of Waferboard Treated with Cross-Linking Reagents
- 2.3 Hygroscopic Properties and Biological Resistance of Medium Density Fiberboard (MDF) Treated with Vaporous Formaldehyde

Conclusion

Acknowledgments

References

Introduction

One of the most important characteristics of wood is its renewability. It may even be inexhaustible providing that it is used with foresight and long-range planning. In an age of dwindling fossil-fuel resources, alternative resources such as wood which are continuously regenerated by nature become more important. Therefore, necessity of wood research has

*¹ This review article is the abstract of the Ph.D. thesis by the author (Kyoto University, 1996)

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been expanded in industry, government, and academic community. Wood is preferred building or engineering material because it is economical, low energy in processing, strong, and aesthetically pleasing. It has, however, several disadvantageous properties such as flammability, biodegradability, dimensional instability by ambient humidity, and degradability by ultraviolet (UV) light, acids, and bases. These disadvantageous properties can be improved by chemically modifying the cell wall components and/or by filling the substance in the lumen and cellular voids.

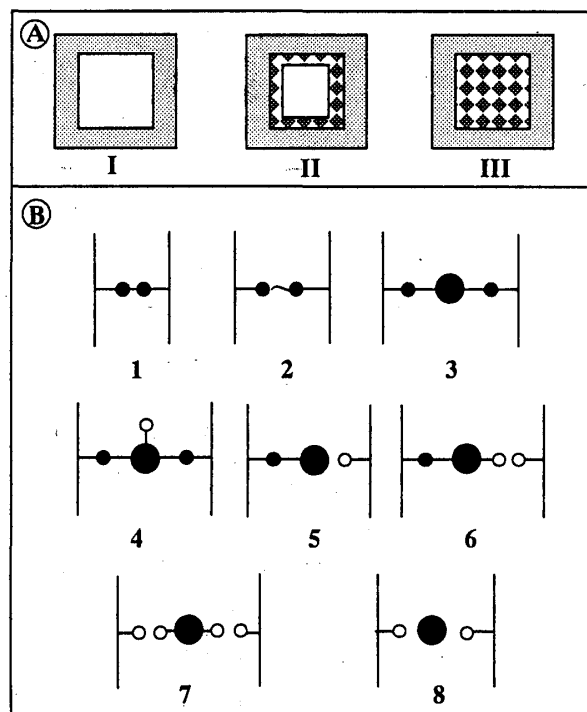
Norimoto *et al.*¹⁾ classified the chemical modification of wood into three categories in cellular and eight categories in molecular levels. These schematic models are shown in the figure. The upper part of the figure represents the model in cellular level: (I) modification of cell wall only, (II) deposition on cell lumen surface, (III) filling of lumen.

Most of the preservative treatments of wood against biological attack are achieved by the deposition of toxic reagents in the cell walls and on the cell-lumen surface and categorized into type II, because toxic chemicals such as chromated, copper, arsenate (CCA) is permeable into the pores of cell lumina and cell walls. In the type II, biological resistance could be attained by the impregnation of low molecular phenolic resin instead of toxic reagents. However, the high molecular resin-treated wood such as conventional wood-plastic-combination (WPC) was so often attacked by decay fungi, because the plastic resin only encrusted the cell lumina without any deposition or modification of the wood cell walls.

The type I has been scarcely applied to the prevention of biodeterioration of wood except for acetylation. The treatment of type III is represented by 7 or 8 in lower part of the figure. That is, the reagent has hardly chemical interaction with cell wall components. Because the leaching of toxic reagent from the cell lumen is often serious from the viewpoint of environmental pollution, it is desirable to modify the wood by the types I in which any reagent is chemically bound to the wood components.

The acetylation, which belongs to the type 5, is one of the typical chemical treatments to enhance the dimensional stability of wood. The introduced acetyl groups or remaining by-product of acetic acid itself do not have toxicity, but the acetylated wood shows high resistance to volumetric change and biological attack. This is partly attributed to the lowering of equilibrium moisture content of wood, namely the worsening of water uptake for decay fungus, and to the introduction of inert groups, which prevent the enzyme system from break down of wood components.

Many types of chemical treatment to improve the dimensional stability have been reported until now. Among them, types 1 to 4 in the figure are characterized to be cross-linking formation. The typical treatment of type 1 and 2 are formaldehyde treatment (formalization) in vapor phase and liquid phase, respectively. By the vapor phase formalization, high dimensional stability can be obtained. On the other hand, the liquid



Model of chemical modification of wood. A, cellular level; (I) modification of cell wall only, (II) deposition on lumen surface, (III) filling up of lumen. B, modification of lignocellulosic material at molecular level. Empty circles, hydroxyl group available for hydrogen bonding; small filled circles, substitution of hydroxyl group; large filled circles, bulking agent (cited from Norimoto *et al.*¹⁾, with permission).

phase formalization is not effective to increase the dimensional stability but, it can improve the wrinkle resistance and permanent press properties of cotton fabrics. However, the biological resistance of formaldehyde treated wood has not been studied in detail until now.

Types 3 and 4 are also characterized by the other cross-linking reaction but the other functional group is introduced in type 4. Typical reagents of type 3 are difunctional aldehydes such as glyoxal and glutaraldehyde those which molecular weights are larger than formaldehyde. They are utilized for the secondary processing of cotton fabrics that penetrate into cell wall and form the cross-linking between cell wall components. The treatment with dimethylol-dihydroxy-ethyleneurea (DMDHEU) as a low-formaldehyde reagent, which belongs to type 4, is the most popular cross-linking reagent in textile industry.

Because these non- or low-formaldehyde cross-linking reagents have not been applied to wood, their effects on the biological resistance of treated wood have not been thoroughly investigated until recently. However, the detrimental effect of liberated formaldehyde to human body is more and more taken seriously, and these alternative non- or low-formaldehyde reagents are more promising in the future, if they successfully react with wood components.

In the present study, application of several cross-linking reagents to the chemical treatment of wood were investigated especially on the viewpoint of the protection from biological attacks. This concept is targetted to make the attacking conditions just unfavorable without killing of causal decay fungi and termite.

The improvement of weathering property is also important, because the water proofing or hydrophobic properties of wood-based materials is much related to the dimensional stabilizing effect.

In the first chapter of this study, properties enhancement of solid wood through several cross-linking formations was investigated. The effects of formaldehyde cross-linking to the attacks by decay fungi and subterranean termites were dealt in Section 1.1. Those of the non- and low-formaldehyde reagents, namely glyoxal, glutaraldehyde, and DMDHEU were described in Section 1.2. In Section 1.3, the protective effects of these treated woods to the weathering, irradiation of sunlight or artificial ultraviolet light, were described.

The second chapter deals with the application of cross-linking treatment to the reconstituted wood materials such as laminated-veneer-lumber (LVL), waferboard, and medium-density fiberboard (MDF). For the world demand, to save forest resources, the production and utilization of these materials should be more increased. It is as a matter of course that the dimensional stability, biological resistance, and any other mechanical and physical properties should be evaluated when these materials are applied to the structural members of wooden constructions. Even when any chemical treatment is successfully applied to the small-scale wood elements, some unexpected drawback may occur in the production of reconstituted wood. In this part, chemically treated LVL (Section 2.1), waferboard (Section 2.2), and MDF (Section 2.3) were expected to the water soaking, sunlight irradiation, and biological attack and evaluated in resisting to these deteriorating agents. The successful application of these chemical treatment to the reconstituted wood products will open up the new and efficient utilization of forest resources.

Chapter 1 Properties Enhancement of Solid Wood by Cross-Linking Formation

1.1 Biological Resistance of Formaldehyde-Treated Wood

1.1.1 Introduction

Formalization is the cross-linking reaction between formaldehyde and hydroxyl groups of cellulose, hemicellulose, and lignin. The reaction scheme was proposed as follows in Scheme 1.1.



Scheme 1.1. Proposed linkage between formaldehyde and wood hydroxyl groups.
Where wood-OH implies hydroxyl groups of wood components.

The formalization has been applied to wood and paper as a method of dimensional stabilization. Recently, it was reported that the treatment was effective also for the improvement of acoustic property of the wood for musical instruments²⁾. While, some workers have earlier pointed out the improved decay resistance of formaldehyde-treated wood³⁻⁶⁾. However, none of them dealt with the relation between the enhanced decay resistance and the degree of treatment or possible mechanism of decay inhibition. Also the effect of formalization on the termite attack against wood has never been reported.

Meanwhile, the method of vapor phase formalization was improved to control arbitrarily the degree of reaction with high reproducibility⁷⁾. The conventional method of formalization catalyzed by hydrogen chloride or various metallic chloride often causes a severe loss of mechanical strength in the treated woods. Wilson and others⁸⁾ applied sulfur dioxide (SO₂) as the alternative catalyst to the formalization of cotton fabrics, and the effectiveness was also confirmed to the treatment of wood⁹⁾.

In this chapter, the effect of the formalization in both vapor and liquid phase on resistance against to the fungal and termite attacks were described, and the enhancing mechanism of decay resistance through the treatments were discussed. Especially, the liquid phase formalization was considered worthy to examine, since the reaction proceeds at room temperature in a simple process without a serious strength loss.

1.1.2 Materials and methods

Materials

Two species of softwood, western hemlock (*Tsuga heterophylla* Sarg) and sugi (*Cryptomeria japonica* D. Don), and two species of hardwood, albizzia (*Paraserienthes falcata* L. Fosc) and buna (*Fagus crenata* Blume), were used. Sapwood blocks measuring 20 mm (T) × 20 mm (R) × 10 mm (L) were prepared from each wood species.

Vapor phase formalization

The vapor phase formalization was carried out according to the method of Minato and Yano⁹⁾ as shown in Fig. 1.1. Technical grade tetraoxane cyclic tetramer of formaldehyde ((CHO)₄) was used as a vapor source of formaldehyde. The reaction was catalyzed by 99.9% of SO₂ which was supplied from commercial bomb. Twenty pieces of specimen were pre-heated in a 3.5-liter glass vessel for 20 min. at 120°C under the reducing pressure until about 12 mm Hg. After 3 g of tetraoxane and 400 ml of SO₂ were added, the vessel was heated for 2 to 24 hrs at 120°C in an oven. The treatment was duplicated under the same condition.

Liquid phase formalization

The liquid phase formalization was conducted according to Pierce *et al.*¹⁰⁾. Blocks of sugi and buna were immersed in about 1 liter of reaction mixture consisting of 3.6%-formaldehyde, 3.7%-hydrogen chloride, 75.0%-acetic acid, 17.7%-water at room temperature for 1 to 4 days. After treatment, the specimens were thoroughly rinsed by

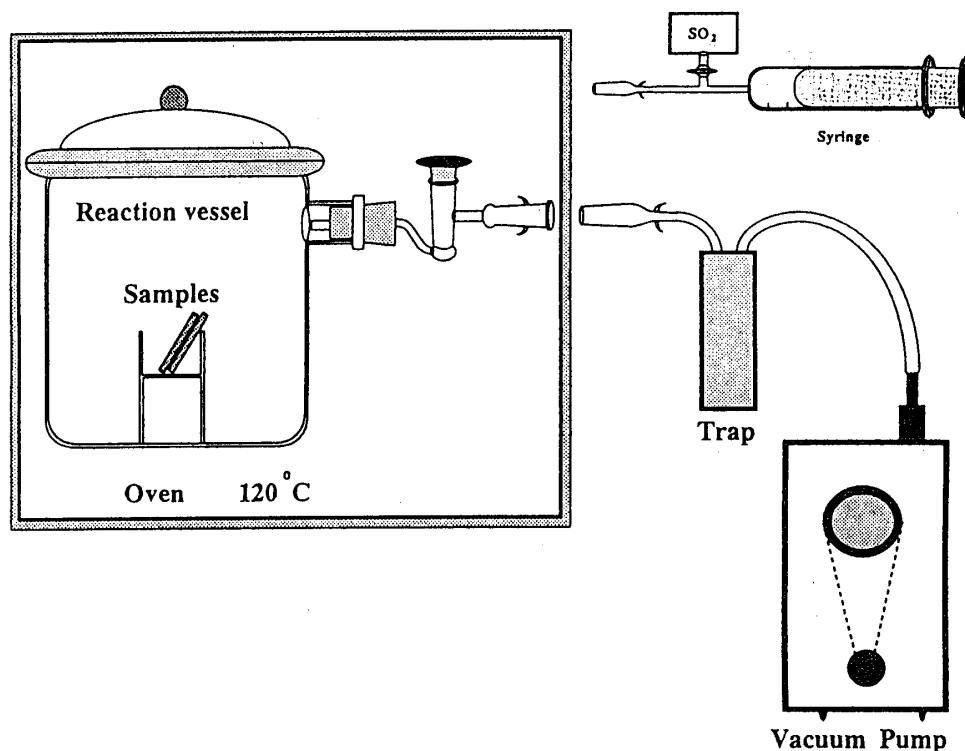


Fig. 1.1. Equipment for the vapor phase formalization.

running water for several days.

Measurement of dimensional stability

The specimens were soaked in water and aspirated until the specimens have sunk at the bottom. They were then dried in the oven at 60°C for 3 days. The dimension in swollen-state and in oven-dried state were determined using a micrometer (0.01 mm unit) to calculate the volumetric swelling coefficient (S). From the difference of swelling for the treated and the untreated specimens, an antismelling efficiency (ASE) was calculated. These calculation equations by Tarkow and Stamm¹¹⁾ are as follows:

$$S (\%) = \{(V_2/V_1) - 1\} \times 100$$

where V_2 is the specimen volume in swollen state, and V_1 is that in oven-dried state.

$$ASE (\%) = \{1 - (S_2/S_1)\} \times 100$$

where S_2 is the volumetric swelling coefficient of the treated specimen, and S_1 is that of untreated one.

The weight gain (WG) in percentage was obtained from the oven-dried weight before and after the treatment.

Decay resistance tests

1) Mono-culture decay test was conducted according to Japan Wood Preserving Association (JWPA) Standard No. 3-1992, using a brown-rot fungus *Tyromyces palustris* (Berk. et Curt.) Murr. - FFPRI-0507 and a white-rot fungus *Coriolus versicolor* (L. ex Fr.)

Quél.-FFPRI-1030. The test blocks were sterilized in gaseous ethylene oxide after measuring their original dry weights. The blocks in the glass jars were kept at 28°C and exposed to fungal attack for 12 weeks. The extent of attack was determined based on the percent of weight loss (WL). Also, the moisture content (MC) of each block was measured immediately after removal from the glass jar.

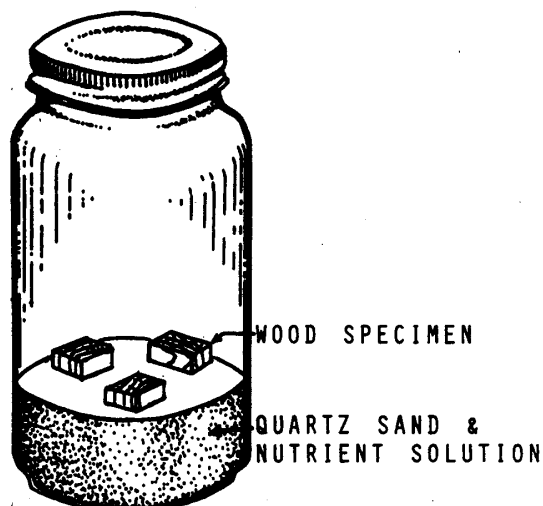


Fig. 1.2. An assembled soil block test according to JWPA No.3-1992.

2) The soil-burial test was also made to evaluate the resistance against various soil-inhabiting microorganisms, particularly soft-rot fungi and some wood-attacking bacteria. Blocks were buried in a moistened unsterilized soil enriched with humus. The test was carried out at 28°C for 9 months which enabled the severe degradation of untreated blocks.

Termite resistance test

The test block were subjected to subterranean termites in according with JWPA Standard No. 12-1992. *Coptotermes formosanus* Shiraki and *Reticulitermes speratus* (Kolbe) were used for the test. One each of the untreated and treated test blocks were placed at the bottom of a test container, an acrylic vessel with one end sealed with hard plaster of Paris to form a 5 mm thick bottom. One hundred and fifty workers from each species of termite were subjected to the forced-feeding test. Fifteen and five soldiers of *C. formosanus* and *R. speratus* were introduced together with each species of workers. Test periods were 9 and 3 weeks for *C. formosanus* and *R. speratus*, respectively. Termite mortality (TM) was recorded weekly and the weight loss (WL) by termite attack was calculated at the end of the test.

Scanning electron microscope (SEM) observation

Small sections were taken from wood specimens after decay tests. These samples were mounted on stubs with the fungus-exposed surfaces on the top, and coated with gold for observations by a Hitachi S-500 SEM.

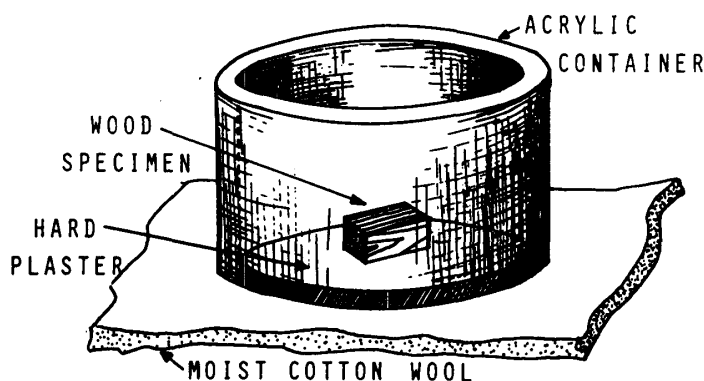


Fig. 1.3. An assembled forced-feeding test according to JWPA Standard No. 12-1992.

^{13}C NMR spectrometry

NMR spectral analysis of treated wood were carried out to confirm the substitution of hydroxyl groups in the wood components after formalization.

CP/MAS ^{13}C NMR measurements at 50 MHz were performed on a JEOL JNM-FX 200 spectrometer using a magnetic field of 4.7T. A MAS rotor containing wood powder was equipped with on O-ring seal.

1.1.3 Results and Discussion

Dimensional stability

Tables 1.1 and 1.2 show the ASE and WG along with the reaction conditions of formalization. In the vapor phase treatment, the reaction did not essentially occur within 2hr, but after that ASE and WG increased with the reaction time. The ASE and WG were highest in albizzia, and lowest in buna. The order of ASE seemed to follow the order of specific gravity of wood species tested.

In liquid phase treatment, the antismelling efficiency was large negative values. This was due to the fact that the specimen in the reaction solution swelled more than in water but they recovered their original dimension similar to the untreated specimen after drying. The negative values do not always mean that the reaction did not occur, because a slight but

Table 1.1. Antismelling efficiency (ASE) and weight gain (WG) of western hemlock and albizzia after vapor phase formalization.

Run No.	React. time (h)	WG (%)	Western hemlock		WG (%)	Albizzia	
			ASE (%)			ASE (%)	
			Radial	Tangential		Radial	Tangential
1	3	2.0	15.4	17.8	1.8	23.0	28.3
2	7	2.3	36.9	39.6	2.9	39.4	44.6
3	12	4.0	50.6	52.0	4.5	54.9	59.3
4	24	4.5	58.4	61.3	6.3	64.1	69.5

Note: Mean values of 40 specimens.

Table 1.2. Antiswelling efficiency and weight gain of sugi and buna after vapor and liquid phase formalization.

Run No.	React. time (h)	WG (%)	Sugi ASE (%)		WG (%)	Buna ASE (%)	
			Radial	Tangential		Radial	Tangential
1	2	-0.99	-2.6	-4.3	-0.06	0.4	4.4
2	5	-0.58	24.8	26.6	-0.06	6.2	11.5
3	10	0.73	49.0	48.7	0.84	23.0	33.6
4	24	1.62	57.0	58.7	0.95	33.3	44.2
5*	24	2.3	-15.9	-20.6	1.03	-24.5	-15.4
6*	96	1.90	-21.9	-24.4	-1.20	-41.4	-32.6

Note: Mean values of 40 specimens. *Carried out in liqued formalization.

significant WG was yielded in spite of the loss in some wood extractives. The evidence of the reaction has also been given by the bending creep test where the liquid phase treatment restrained the deformation of wood to some extent¹⁾. Rowland *et al.*¹²⁾ reported that any restraint of shrinking and swelling was not gained by only a polymeric cross-linking found in the liquid phase reaction.

Decay resistance of treated wood

Weight losses of treated wood in vapor phase after 12 weeks exposure to *T. palustris* are presented in Fig. 1.4. Weight losses of untreated softwood (58% for western hemlock and 38% for sugi) were higher than those of untreated hardwood (23% for albizzia and 28% for buna). This was followed by a general trend reported by Fengel & Wegener¹³⁾ that most of brown-rot fungi prefer to softwood than hardwood.

Effect of vapor phase formalization was very poor against buna which had still 13% WL by *T. palustris* even when it was treated for 24 hr, although decay was completely eliminated in other three species at only 10–12 hr reaction.

The vapor phase formalization was more effective against the white-rot fungus *C. versicolor* (Fig. 1.5). The fungus caused 60% and 44% WLs in the untreated control of western hemlock and sugi, respectively, but decay was eliminated dramatically at only 3 hr reaction for western hemlock, and 5 hr reaction for sugi. As in the case of *T. palustris*, the treatment was not effective for buna which had still 4% WL even at reaction time of 24 hr.

The higher resistance of formaldehyde-treated softwood than hardwood might be related to a different extent of substitution of hydroxyl group as proposed in acetylated wood. Takahashi *et al.*¹⁴⁾ speculated that different reactivities between softwood lignin (guaiacyl type) and hardwood lignin (rich in syringyl type) existed in acetylation, because a easier fixation of CCA to guaiacyl lignin has been reported by a few investigators.

The different decay-inhibiting effects of formalization in decay types, brown-rot and white-rot, were also reported by Schmidt⁶⁾. As a reason, he thought that the white-rot

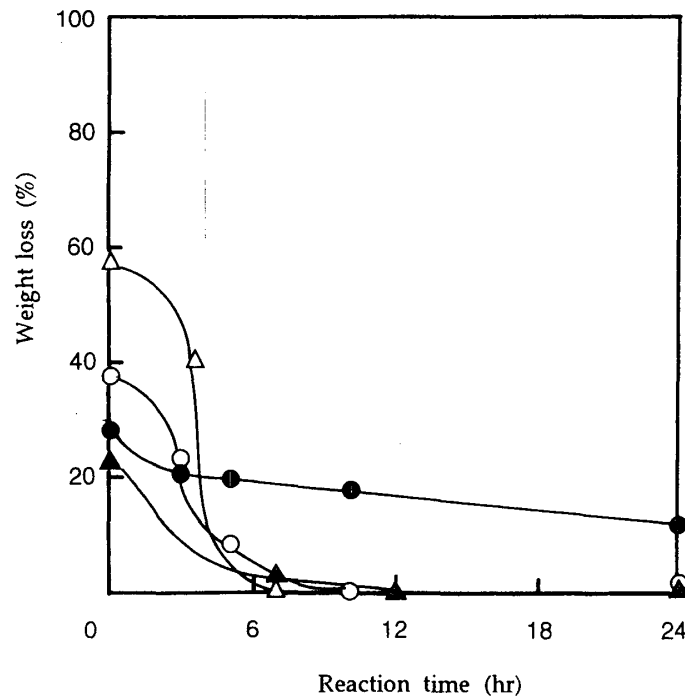


Fig. 1.4. Weight loss of formaldehyde-treated wood in vapor phase after exposure to brown-rot fungus *Tyromyces palustris* for 12 weeks.
Legend: △: Western hemlock, ○: Sugi, ▲: Albizzia, ●: Buna.

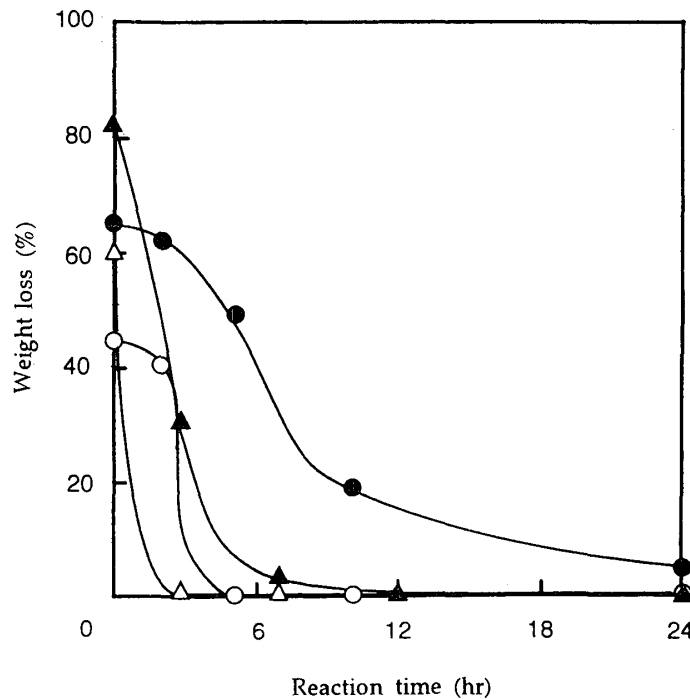


Fig. 1.5. Weight loss of formaldehyde-treated wood in vapor phase after exposure to white-rot fungus *Coriolus versicolor* for 12 weeks.
Legend: See Fig. 1.4.

fungus breaks methylene linkages of lignin, and releases a free formaldehyde which disinfects the fungal attack. However, this seems to be questionable, because in this study, the decay resistance differ significantly between hardwood and softwood, although the similar amount of free-formaldehyde should remain in the treated wood irrespective of wood species.

Similar trend was observed also in acetylated wood¹⁵⁾, in which the difference was explained by the preferential substitution of hydroxyls on lignin with acetyl group at the low level of acetylation as stated by Rowell¹⁶⁾. The higher resistance of formaldehyde-treated wood against white-rot fungi than brown-rot fungi was also considered to be caused by the substitution of oxymethylene linkages in lignin. The similar results were observed in the acetylated wood against white-rot fungi¹⁴⁾. They reported that a possible contribution of lignin substitution on the higher resistance of acetylated softwood to white-rot fungi. As is generally known, lignin is decomposed simultaneously with polysaccharides and its decomposition is always essential for their decay activity for white-rot fungi. Therefore, highly substituted lignin hydroxyls make acetylated wood more resistant to white-rot fungi than to brown-rot fungi which can decompose poly-saccharides selectively leaving lignin in almost intact.

Though such selectivity of the reaction among wood components is not found yet for the formaldehyde-treated wood, it is well-known that lignin reacts with formaldehyde and can be cross-linked¹⁷⁾ and there should be a possibility of different distribution of oxymethylene linkage on formaldehyde-treated wood between softwood and hardwood.

An alternative explanation to the differences of decay inhibiting effect between brown-rot and white-rot fungi is based on the reaction of cellulolytic enzymes. Wilcox¹⁸⁾ reported that the action of the cellulolytic enzymes of a white-rot fungus was restricted to cell wall surface, while those of brown-rot fungus were able to penetrate and act within the cell walls. If this is true, the treated wood can resist against the attack of *C. versicolor* at lower reaction level than that of *T. palustris*, because a cross-linking initiated from the lumen surface¹⁹⁾.

Results of soil-burial test for vapor phase formalization are shown in Fig. 1.6. The treatment yielded a complete decay elimination of sugi even at 5 hr, the shortest reaction time tested. In the case of buna, the treatment was rather slow-acting but it could virtually eliminate decay at 24 hr reaction. The curves of decay inhibition were similar to those of *C. versicolor* (Fig. 1.5), indicating that both soft-rot fungi and white-rot fungi might response in similar manner to formaldehyde-treated wood.

As shown in Fig. 1.7, control block was much infested fungal hyphae and was seriously destroyed but treated block had not any sign of microbial invasion.

The liquid phase formalization did not affect the decay resistance of sugi and buna against brown-rot fungus of *T. palustris* (Fig. 1.8a). However, when exposed to the white-rot fungus of *C. versicolor* (Fig. 1.8b) and unsterilized soil (Fig. 1.8c), the effect was remarkable, especially for sugi. Decay was eliminated at 24 hr reaction shorter time.

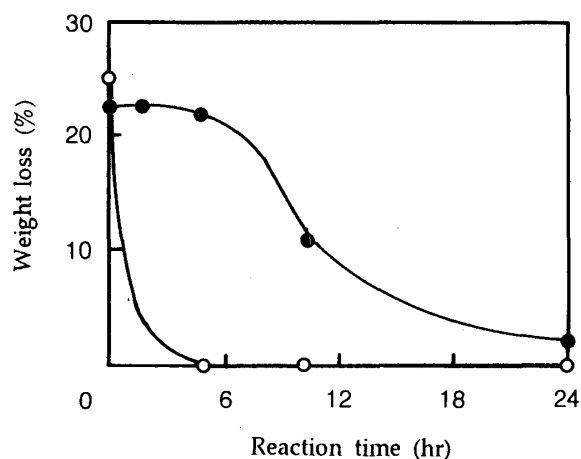


Fig. 1.6. Weight loss of formaldehyde-treated wood after exposure to soil microorganisms for 9 month.
Legend: See Fig. 1.4.

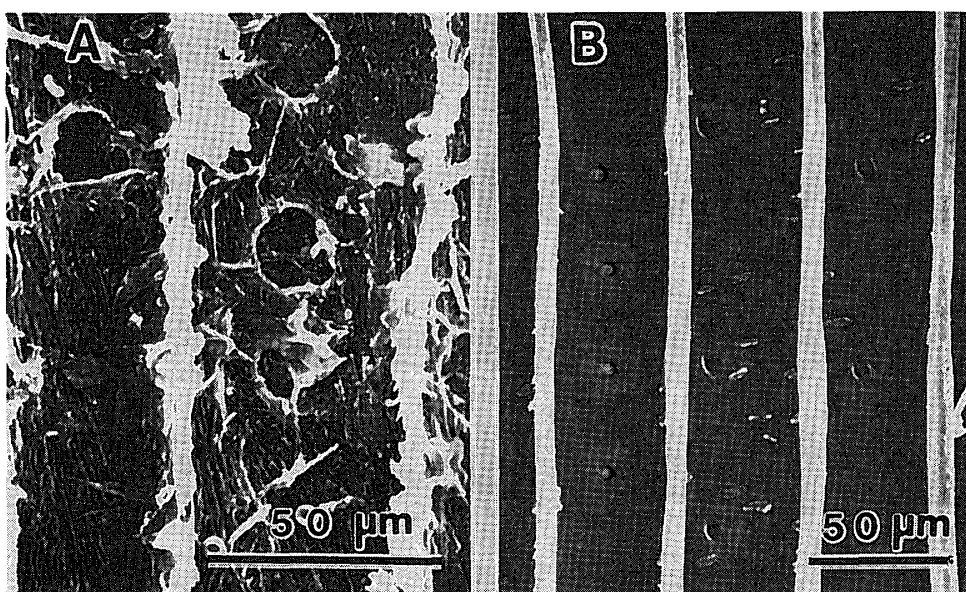


Fig. 1.7. Scanning electron micrographs of untreated (A) and formaldehyde-treated sugi tracheids (B) after 9-month exposure in unsterilized moist soil.

Table 1.3 shows the MC of test blocks after exposure to decay fungi. In any wood species, MCs of untreated and treated blocks exposed to *T. palustris* were higher than those to *C. versicolor*. This trend has been generally accepted as a different physiological characteristics between the two types of decay fungi. Over-all higher MC values of albizzia blocks than those of other wood were probably due to the low specific gravity of albizzia. In all fungus-wood pairs, MC decreased roughly with the increase of reaction time in vapor phase treatment, and with the resultant decline of decay. The liquid water in wood blocks might be derived from metabolic breakdown of cell wall components, transportation by

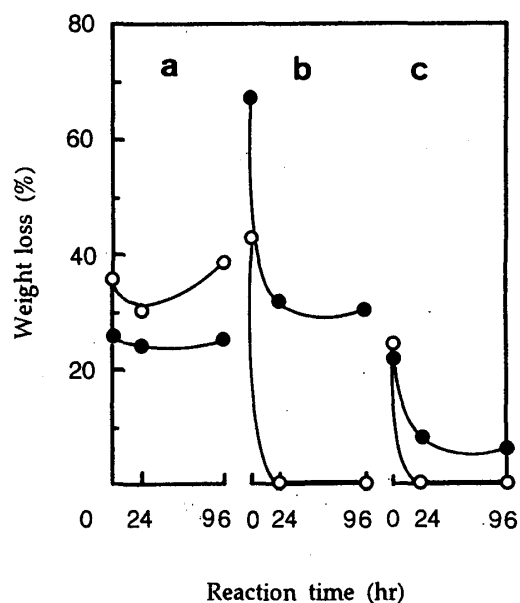


Fig. 1.8. Weight loss of formaldehyde-treated wood in liquid phase after decay for 12 weeks by *Tyromyces palustris* (a), *Coriolus versicolor* (b), and soil burial test (c) for 9 months.
Legend: See Fig. 1.4.

Table 1.3. The moisture content of specimens after exposure to decay fungi.

React. time (hr)	<i>Coriolus versicolor</i>				<i>Tyromyces palustris</i>		
	Sugi	Buna	Western hemlock	Albizzia	Sugi	Buna	Western hemlock
0	66.9	59.1	135.0	252.2	348.3	326.2	450.6
2	63.4	46.4	—	—	336.9	297.4	—
3	—	—	101.5	181.4	—	—	98.9
5	59.1	52.7	—	—	112.5	194.0	—
7	—	—	78.8	163.2	—	—	78.0
10	56.4	59.5	—	—	93.0	90.4	—
12	—	—	62.4	124.3	—	—	78.8
24	44.4	59.4	58.4	78.9	75.0	65.3	64.3
24*	65.2	54.4	—	—	139.4	140.6	—
96*	67.6	54.2	—	—	141.1	135.5	—

Note: Mean values of 9 specimens. *Carried out in liquid formalization.

penetrating fungal mycelium and/or capillarity movement of nutrient solution.

Even in the highly treated wood, a few cells adjacent to the specimen surfaces were sometime colonized with fungal hyphae (Fig. 1.9). However, they decreased in the cells locating in the inner part of the specimen. The hyphae were able to invade easily and colonize into the surface cells contact with fungal mat growing on nutrient medium. The supply of nutrient source from the medium might enable the fungal penetration into the

wood cells at a limited depth from the surface. However, in the inner part of treated block, fungal hyphae might be unable to take any nutrient from the breakdown of formalized cell wall and this might retard the subsequent invasion into the deeper cells of the specimen.

Relationship between dimensional stability and decay resistance

Figure 1.10 show the WL versus ASE relationships for sugi (a) and western hemlock (b) which were formaldehyde-treated in vapor phase for different reaction periods. Decay of these treated woods was eliminated at ASE between 40 and 50% for *T. palustris* and 20 and 30% for *C. versicolor*. When referring from the previous reports on acetylated wood²⁰⁾, the WLs caused by *T. palustris* and *C. versicolor* were almost undetectable at over 60 and 50 % of ASE, respectively. In acetylated wood, the replacement of the active hydroxyl-units to the stable acetyl units should contribute to the enhancement of dimensional stability and biological resistance, while the formation of cross-linking between these hydroxyl units should provide the wood the same effect in the case of formaldehyde treatment.

Biodeterioration of wood is considered to be the concerted action of the individual enzyme systems responsible for cellulose, hemicellulose, and lignin decomposition. Therefore protective effect of chemical modification may be attributed to its blocking effect of

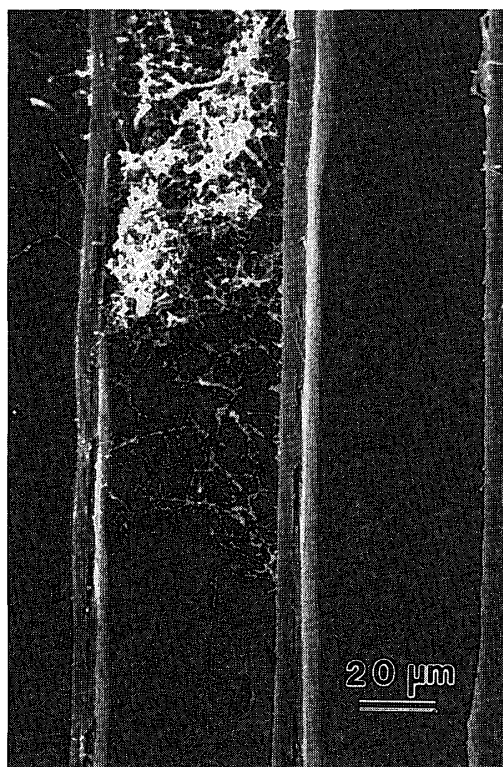


Fig. 1.9. Scanning electron micrograph of sugi tracheids at the surface portion of treated block after exposure to *Tyromyces palustris*. The cell lumina allowed to colonization with fungal hyphae, but the cell walls were not destructed and maintained the intact conditions.

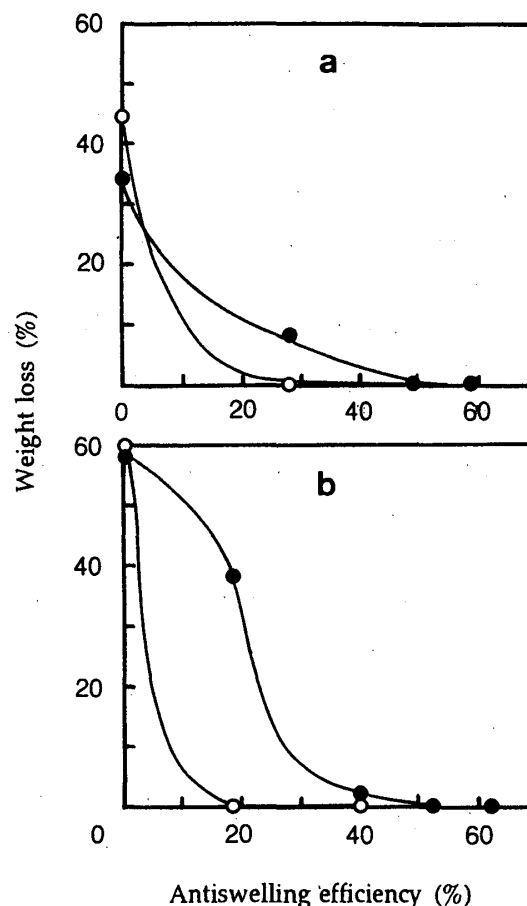


Fig. 1.10. The relationship between antismelling efficiency and weight loss of formaldehyde-treated sugi (a) and western hemlock (b) after exposure to fungi for 12 weeks.
Legend: ●: *Tyromyces palustris*, ○: *Coriolus versicolor*.

enzymatically-reactive sites in these components. Even though, these enzymatically-reactive sites were completely blocked by cross-linking formation, the treated wood was considered to cause some dimensional change as shown in Fig. 1.11.

On the contrary, the bulking of the cell walls was said to be the major effect to increase dimensional stability in the acetylation treatment. The wood acetylated at the level to eliminate the decay attacks should hardly swell exceeding the relatively larger dimensions, and ASE might reach the high value at these stages.

Termite resistance of treated wood

Weight loss of the blocks treated in vapor phase after forced-feeding test by termites are shown in Fig. 1.12. The features of blocks exposed to *C. formosanus* and *R. speratus* after forced-feeding test are shown in Fig. 1.13 together with those from choice test by *C. formosanus* in which blocks were placed around the nest of laboratory colony. In case of destructive *C. formosanus*, complete elimination of attack was not gained in any treated wood,

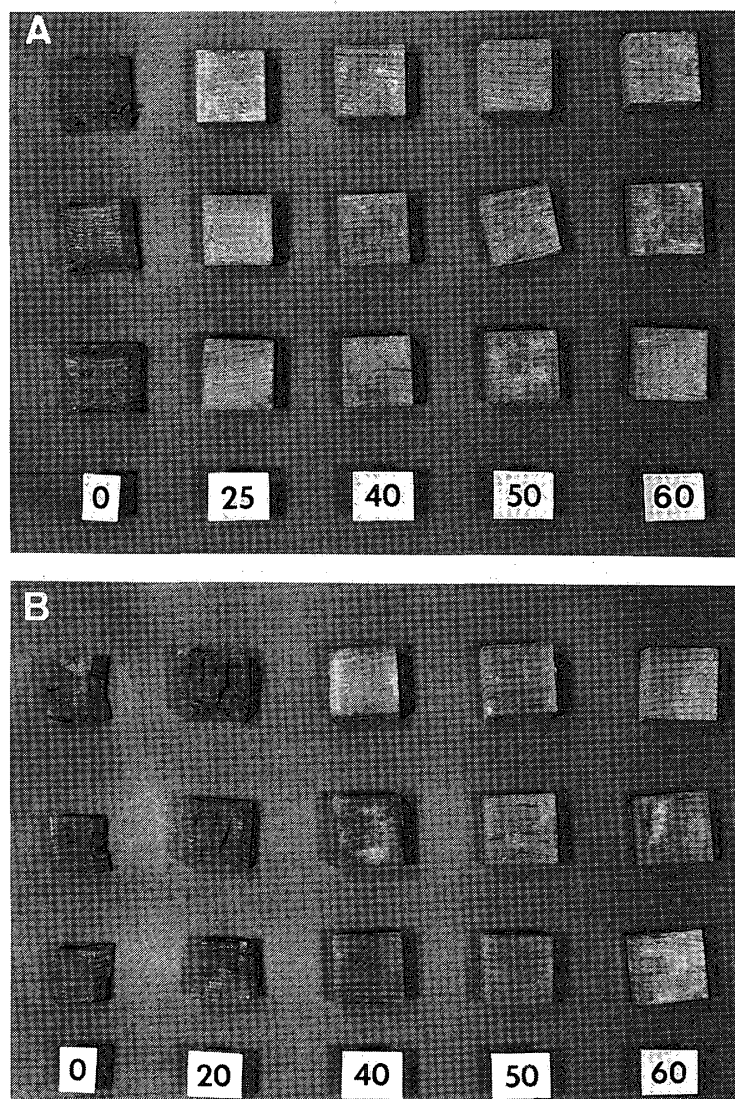


Fig. 1.11. The vapor-phase formaldehyde-treated western hemlock after decay test of *Coriolus versicolor* (a) and *Tyromyces palustris* (b) for 12 weeks.

Note: The numbers for the bottom show the values of ASE.

but the effect of vapor phase formalization was clearly demonstrated in sugi, western hemlock and buna. Albizzia was not much attacked even at untreated control but it was still attacked in spite of the increased reaction times.

Another subterranean termite *R. speratus* has lower feeding-ability of wood in nature than *C. formosanus*. Excepting albizzia, their attack was completely inhibited by the vapor phase treatment (Fig. 1.12b). The easier inhibition of attack by this termites was demonstrated also in the acetylation¹⁵⁾ using forced-feeding and choice-feeding tests. The reason for the present unsuccessful result with albizzia is not understood yet. However, different from the decay resistance, the effect of vapor phase formalization on termite resistance was rather independent on wood species.

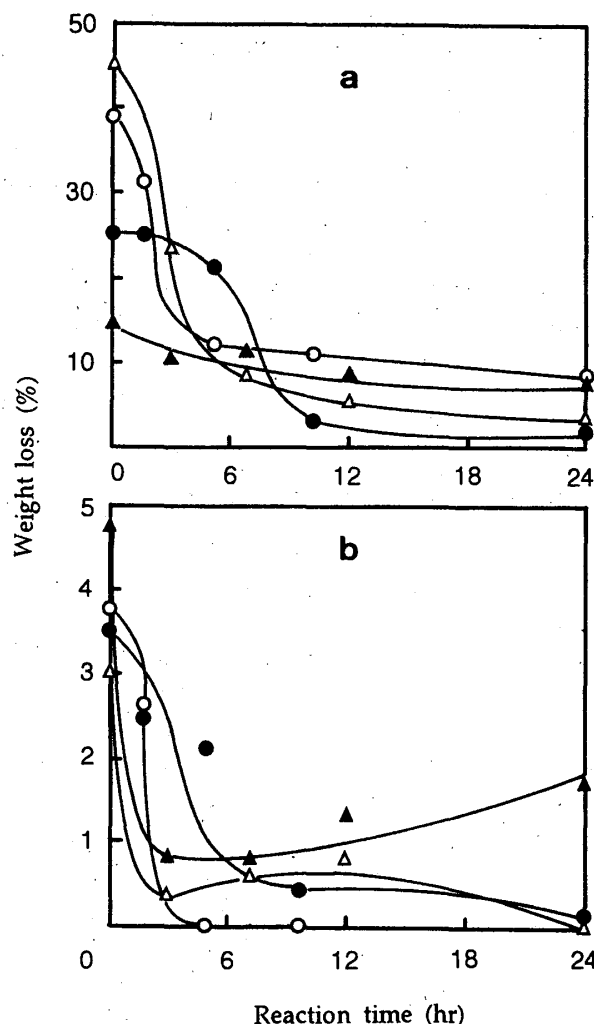


Fig. 1.12. Weight loss of formaldehyde-treated wood in vapor phase after exposure to *Coptotermes formosanus* for 9 weeks (a), *Reticulitermes speratus* for 3 weeks (b).
Legend: See Fig. 1.4.

The liquid phase formalization also could enhanced the termite resistance of wood especially inhibiting the attack by *R. speratus* (Fig. 1.14). However, *C. formosanus* still attacked sugi blocks even when they subjected to the treatment for 96 hr.

The mortality curves of termites fed on formaldehyde-treated sugi and buna are presented in Figs. 1.15 and 1.16. In the case of sugi, all treatments always caused the higher TMs of worker of *C. formosanus* than those of untreated control and starvation, and TM reached 100% by 9 weeks (Fig. 1.15a).

The TMs curves were not necessarily dependent on reaction time and method of treatment, but TMs of 24 hr vapor phase treatment kept the higher values than those of other treatments. While in the case of buna, the difference of TM between vapor and liquid phase treatments was clearly exhibited (Fig. 1.15b). Although TMs of *C. formosanus*

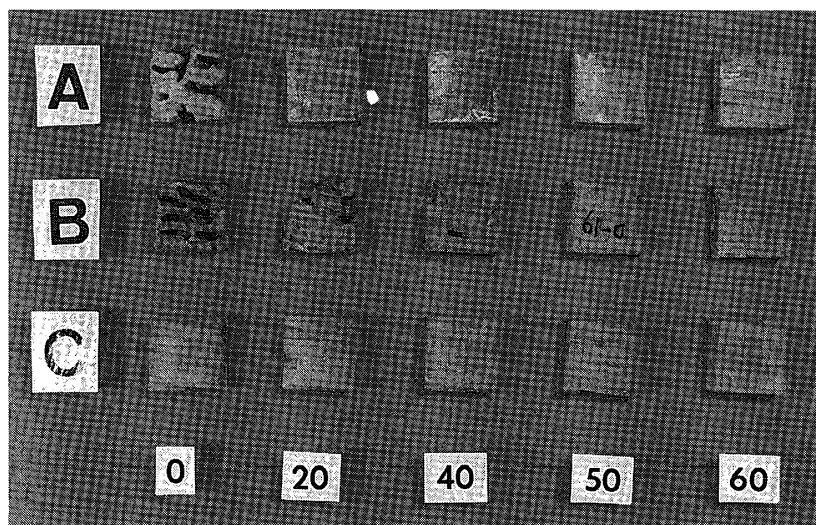


Fig. 1.13. The formaldehyde-treated sugi in vapor phase after attack to subterranean termite.
 Legend: A: Choice tests with *Coptotermes formosanus*, B: Forced-feeding tests with *Coptotermes formosanus*, and C: forced-feeding test with *Reticulitermes speratus*.
 Note: The number at the bottom show the values of ASE.

workers fed on buna treated in vapor phase reached 100% in earlier weeks than those of sugi. TMs of buna treated in liquid phase were always lower than those of sugi.

R. speratus was generally far sensitive to any treatment than *C. formosanus*. All workers of *R. speratus* on any treated wood were dead between 2 and 4 weeks.

Change of protozoan fauna in the intestines of the workers can also be used for clarifying the effect of formalization. The survived termites of *C. formosanus* fed on treated wood and untreated wood for 1 week were compared to examine the changes of the protozoa after squashing out their hindguts. Three kinds of protozoa, *Pseudotrichonympha grassii*, *Holomastigotoides hartmanni* and *Spirotrichonympha leidy* were present in the sound termites. In the intestine of the worker termite fed on treated wood, the number of protozoa decreased greatly and the largest forms of the protozoa, *P. grassii*, disappeared completely. The change of protozoan fauna was similar to that of termites fed on acetylated wood²⁰⁾.

The digestive system of *C. formosanus* termites has been recently investigated by Yoshimura²¹⁾ and he evidenced the great role of symbiotic protozoa in that system. It has been pointed out that cellulose in wood was much depolymerized by the largest protozoa *P. grassii* after partial decomposition by termite itself. Treated wood is eaten by the termites and transferred into their intestines, but it might be resistant to any cellulolytic system in termites. As a results, the termites were not able to obtain any nutriment from the breakdown of the wood and thus lost their vitality.

NMR analysis

The ^{13}C NMR spectra of formaldehyde-treated sugi are shown in Fig. 1.17 along with resultant ASEs. For comparison, those of acetylated sugi are shown in Fig. 1.18¹⁴⁾. In

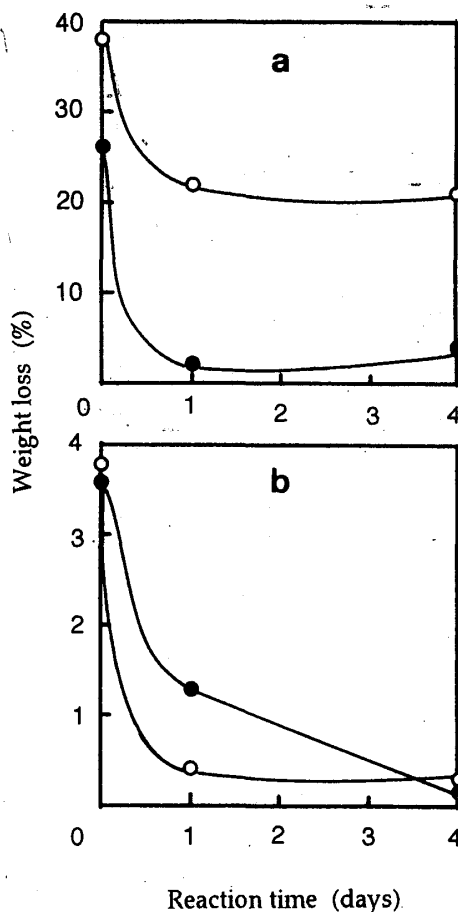


Fig. 1.14. Weight loss of formaldehyde-treated wood in liquid phase after exposure to *Coptotermes formosanus* for 9 weeks (a), and *Reticulitermes speratus* for 3 weeks (b). Legend: See Fig. 1.4.

Fig. 1.18, the low peak at ca. 20 ppm is present in the original non-treated wood (c) and assigned to the acetyl on hemicellulose. The peak C_6 of cellulose original wood is doublet showing crystalline (left) and non-crystalline (right) region. The latter disappeared with acetylation indicating the easier substitution of hydroxyl on the non-crystalline region as reported by Rowell²²⁾.

The rising of the acetyl carbonyl peak was clearly observed again in 175 ppm. The peak between 110–160 ppm are mainly assigned to lignin. The peak at ca. 150 ppm became sharper after acetylation suggesting the peak at possible decreases of free hydroxyl and ether bonds.

In the formalization, signal around 63 ppm which is due to C_6 carbon in the non-crystalline regions of cellulose disappeared and become sharper after formalization, suggesting the possible decreases of free hydroxyl. The peak $C_{2,3,5}$ was different between treated and untreated wood. It indicates that different structure of cellulose caused by formaldehyde reaction with non-crystalline regions of cellulose.

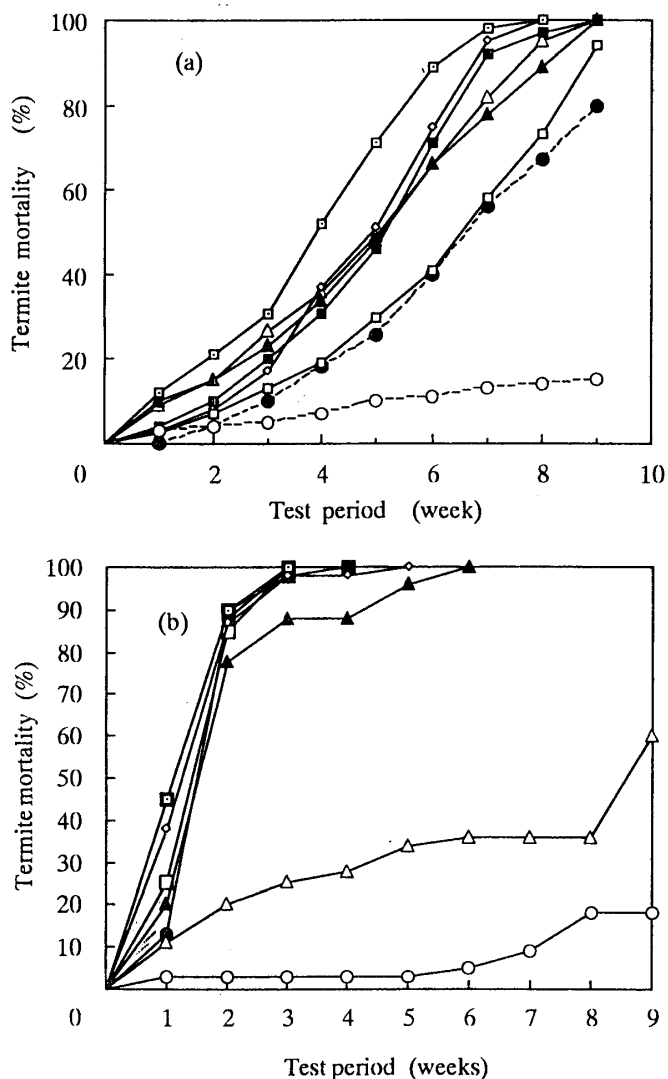


Fig. 1.15. Mortality of worker termite of *Coptotermes formosanus* fed on formaldehyde-treated sugi (a) and buna (b).

Legends: ○: untreated sugi or buna, △: treated in vapor phase for 2h, ▲: 5h, ◇: 10h, and □: 24h, ■: treated in liquid for 24, and ●: starvation.

1.2 Biological Resistance of Wood Treated with Non- or Low-Formaldehyde Reagents

1.2.1 Introduction

Formalization could provide wood with high dimensional stability and resistance against decay fungi and termites as described in Section 1.1. However, vapor of formaldehyde is somewhat toxic to the human body, and therefore special caution should be paid in the processing of formalization. For the chemical processing of cotton fabrics for permanent press and wrinkle resistance, non-formaldehyde cross-linking agents such as glyoxal²³⁻²⁷⁾, glutaraldehyde^{25,28,29)} and low-formaldehyde ethyleneurea type reagents³⁰⁻³²⁾

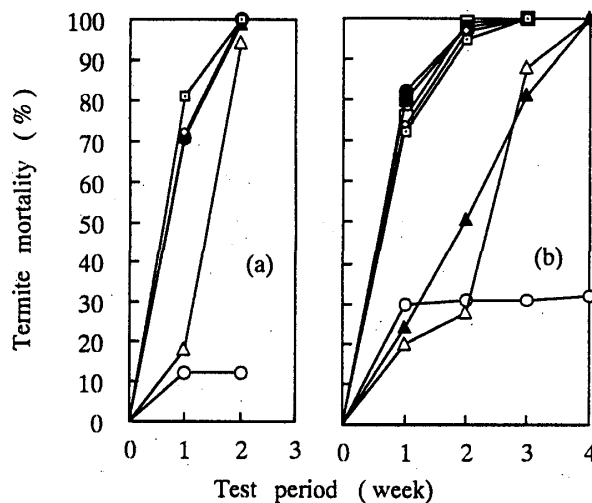


Fig. 1.16. Mortality of worker termite of *Reticulitermes speratus* fed on formaldehyde-treated sugi (a) and buna (b).
Legend: See Fig 1.15.

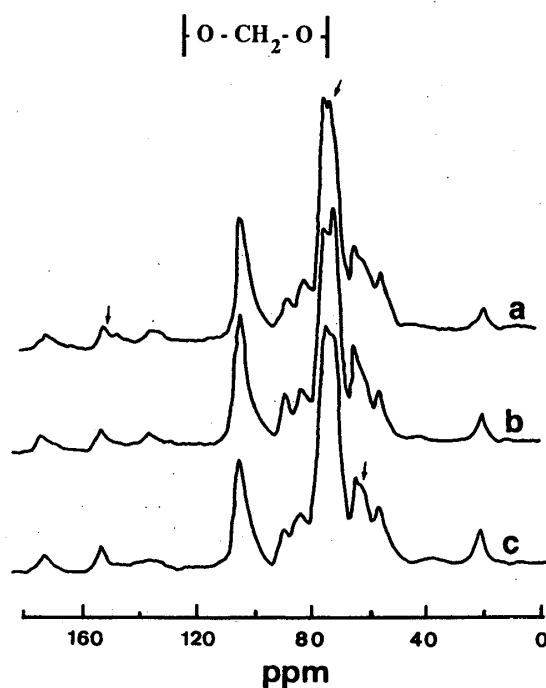


Fig. 1.17. ¹³C NMR spectra of formaldehyde-treated sugi.
Legend: a: 50% of ASE, b: 20% of ASE, and c: Control.

have often been utilized instead of formaldehyde.

By treatment of cellulose with glutaraldehyde ($\text{OHCCH}_2\text{CH}_2\text{-CH}_2\text{CHO}$), or glyoxal (OHCCHO) several cross-linking formations with have been proposed as shown in Schemes

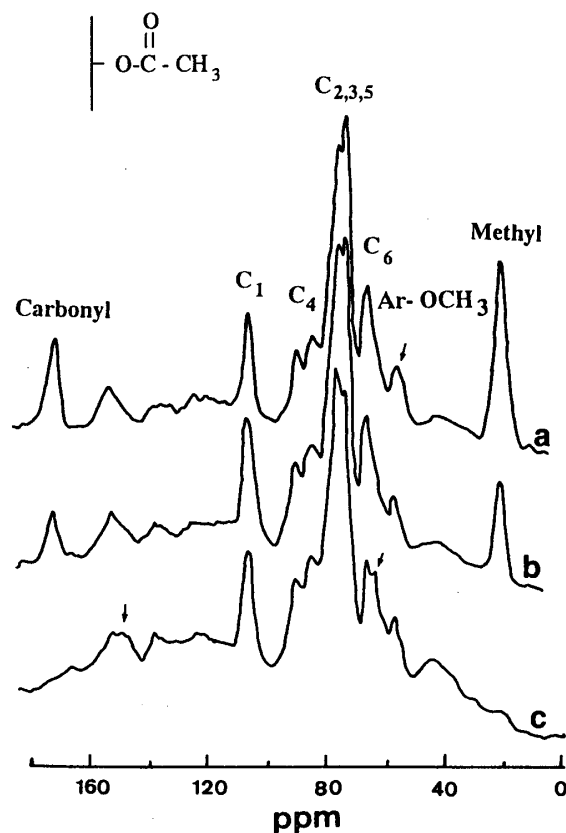
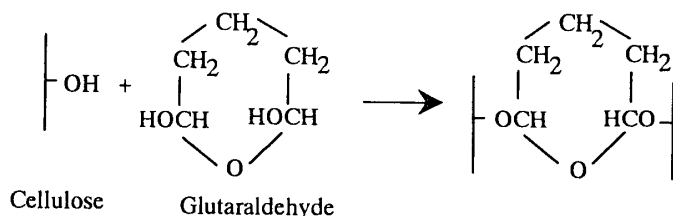


Fig. 1.18. ^{13}C NMR spectra of acetylated sugi (cited from Takahashi *et al.*¹⁴⁾
 Legend: a: 20% of WG, b: 10% of WG, and c: Control.

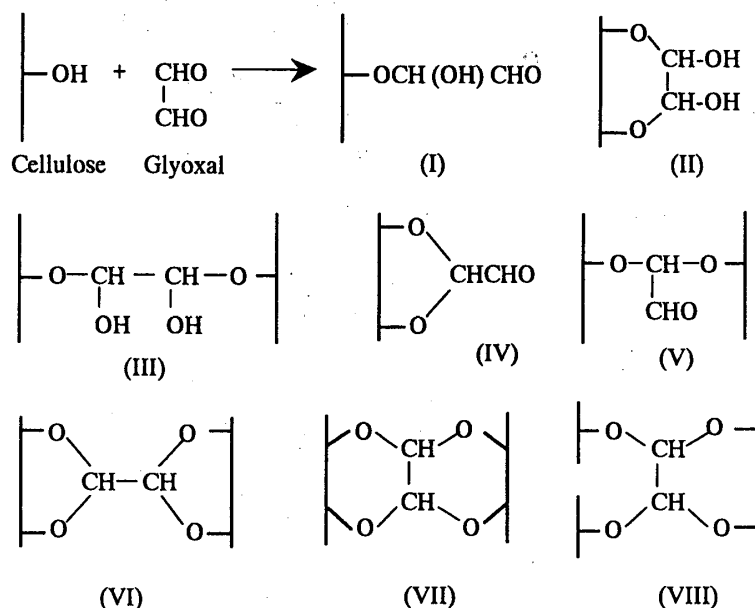
1.2 and 1.3 with comparable effects of formalization have been attained so far. However, because of little durability of the effects, various improvements of the reaction system have been tried. On the other hand, treatments with ethyleneurea type reagents such as dimethylol dihydroxy ethyleneurea (DMDHEU) are thought to be more promising as the alternatives to formalization, although they are not entirely non-formaldehyde (Scheme 1.4). Recently, DMDHEU also was first applied to wood, and great dimensional stabilizing effects were reported³³⁾.

The conventional method of formalization has often caused a serious loss of the mechanical strength of treated wood, because the reaction is catalyzed by a strong acid such

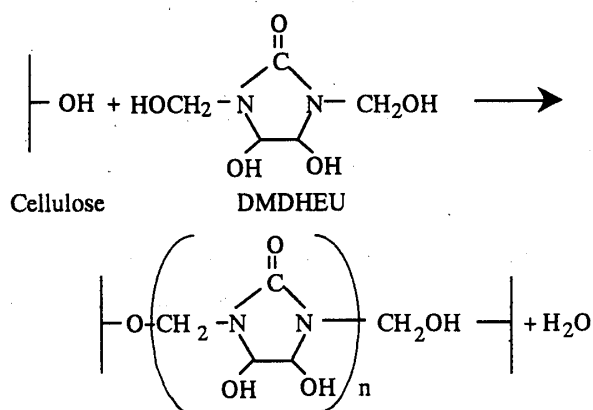


Scheme 1.2. Proposed cross-linking linkages between cellulose and glutaraldehyde (cited from Frick *et al.*²⁵⁾

as hydrogen chloride or various metallic chlorides. Wilson *et al.*⁸⁾ applied SO_2 as an alternative catalyst in the formalization of cotton fabrics, and its satisfactory applicability to wood treatment has been confirmed by Minato and Yano⁹⁾.



Scheme 1.3. Proposed cross-linking linkages between cellulose and glyoxal (cited from Head *et al.*²³⁾)



Scheme 1.4. Proposed linkage between DMDHEU and cellulose (cited from Frick *et al.*³⁴⁾)

In this chapter, SO_2 -catalyzed reactions by the three kinds of non- or low-formaldehyde cross-linking reagents were applied to solid wood, and their effects on biological resistance were evaluated.

1.2.2 Materials and Methods

Chemicals

Reagent grade 40% aqueous solution of glyoxal, 25% aqueous solution of

glutaraldehyde, and technical grade 45% aqueous solution of DMDHEU supplied from Dainippon Ink Co., Ltd. were used as cross-linking reagents.

Materials

Sapwood blocks, measuring 20 mm (T) × 20 mm (R) × 10 mm (L) were prepared from sugi and buna.

Pad-dry-cure treatment

The process was conducted according to the method of Minato and Yasuda³⁵⁾. The blocks were vacuum-impregnated with the respective aqueous solutions of concentrations at 5, 10, 15, 20, and 25% under room temperature. They were kept in the solutions for about one week until they sank to the bottom, and air-dried for 1 week.

Then 10 pieces of test blocks were preheated in a 3.5 liter glass vessel for 20 min. at 120°C, and dried under vacuum. Four hundred ml of gaseous SO₂ was added by a syringe to the glass vessel from a commercial bomb, and the glass vessel was maintained at the same temperature for 24 hr. After treatment, the test blocks were rinsed thoroughly in running water for several days to eliminate the unreacted reagent from the wood.

The WG in percentage were obtained from the oven-dried weights before and after the treatments.

Measurements of dimensional stability, decay and termite resistance

The procedures for these measurements are described in Section 1.1.

1.2.3. Results and Discussion

Weight gain and dimensional stability

The relationships between concentrations of reagent solutions and WGs of wood blocks are shown in Fig. 1.19. WGs increased with increased concentrations of the solutions. WGs at the same concentrations were largest for DMDHEU, followed by glutaraldehyde and glyoxal. Negative WG values were recorded in the glyoxal treatment. It has been pointed out that gaseous SO₂ causes some degradation of wood components when it is used for a catalyst of cross-linking under heated conditions. Negative WG values might be caused by the greater loss of wood components through the treatment than the introduced glyoxal-related linkages, since the molecular weight of glyoxal is very small compared with other reagents tested.

Of the two wood species sugi always gave the higher WGs than did buna at each concentration of treating solution. This was due to the difference of specific gravities and anatomical characteristics between them.

Fig. 1.20 shows the lumen surfaces of sugi tracheid treated with DMDHEU (50% of WG). Even in the two adjacent cells, the lumen of left tracheid (X) had no depositions of reagents with intact condition of warty layer, but that of the right (Y) was fully covered with deposits both around the pit aperture and the unpitted regions.

As discussed in the previous chapter, WGs due to formaldehyde treatment in vapor

As for the dimensional stabilizing effect, these reagents could not give the large relative efficiency (ASE/WG) comparable to the formalization.

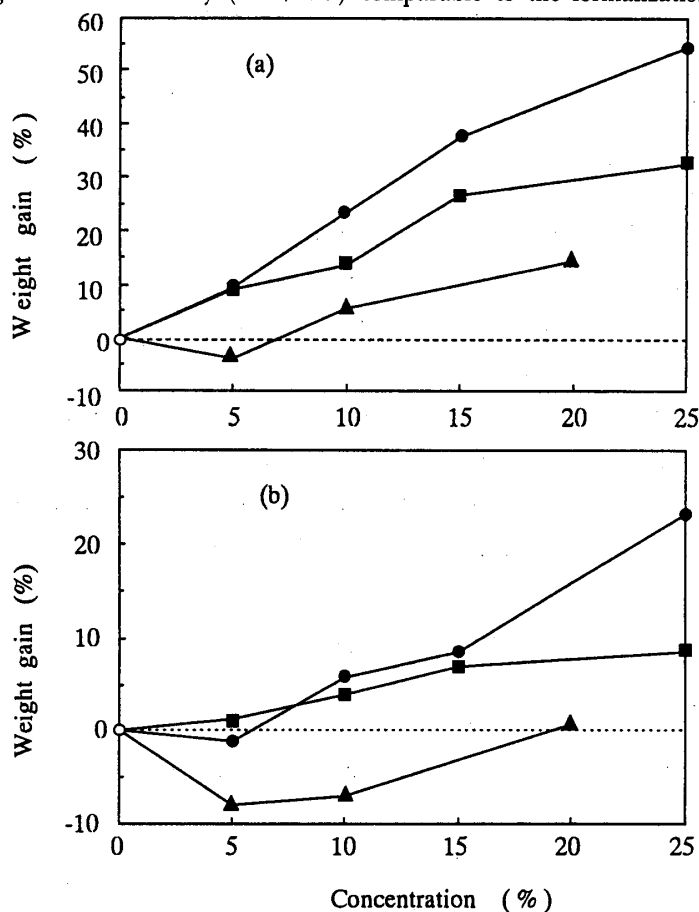


Fig 1.19. Relationship between concentration of solution and weight gain (WG) of treated sugi (a) and buna (b).

Legends: ○: Untreated, ■: Glutaraldehyd, ●: DMDHEU, and ▲: Glyoxal.

phase was extremely small and any modified features by the treatment were hardly detected by SEM observations. However, the pad-dry-cure treatment gave the considerably large WGs and the deposition of reagents were recognized over the lumen surfaces of the treated wood.

As shown in Fig. 1.21, the three treatments yielded different ASE values at the same WGs in both wood species. For example, the glutaraldehyde treatment gave sugi blocks the greatest dimensional stabilizing effect but not so for buna blocks. Dimensional stabilization by these treatments might be achieved by the formation of cross-linking as well as the bulking effect in the wood cell walls³⁶⁾. Therefore, the contributions of these two effects to dimensional stabilization might vary with the type of the chemicals introduced. As for the dimensional stabilizing effect, these reagents could not give the large relative efficiency (ASE/WG) comparable to the formalization.

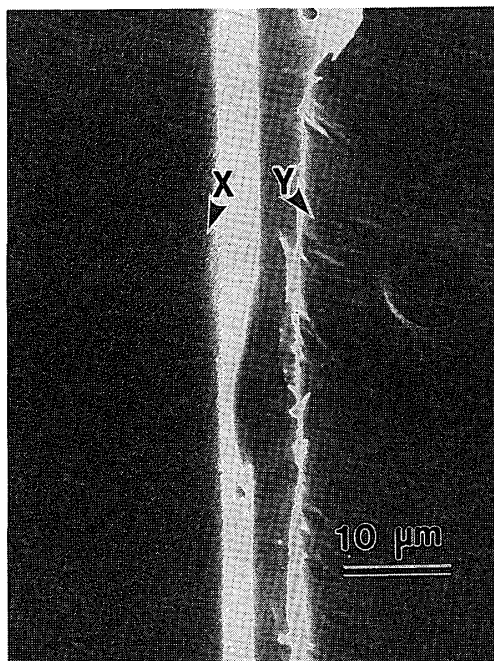


Fig 1.20. The lumen surface of tracheids of DMDHEU-treated wood. The left cell lumen (X) had no deposit of DMDHEU in spite of the full deposits in adjacent cell lumen (Y).

Decay resistance

The results of decay tests are shown in Fig. 1.22. Glutaraldehyde was the most effective in reducing the attacks of sugi and buna by both decay fungi (Fig. 1.22a). Decay was almost nil at more than 10% WGs, which were brought about by the treatment with the smallest 5% and 10% solutions in sugi and buna blocks, respectively. Resultant ASEs from treatments with these solutions were 50 and 30% in sugi and buna, respectively. However, since WL of sugi decreased drastically and reached nil at the smallest WG, it is not possible to decide the minimum values of WG or ASE required to get the complete elimination of decay.

In DMDHEU treatments (Fig. 1.22b), WLs by decay were less than 5% at 10% WG excepting buna exposed to *T. palustris*. As shown in Fig. 1.21, the resultant ASEs at 10% WG were about 50% in both species. When sugi was treated with formaldehyde in the vapor phase, WL by *T. palustris* was no more than 10% even when ASE was only 30%, and it was almost nil at over 50% level of ASE. However, the attacks of *C. versicolor* was inhibited completely even at low level of ASE as 20% by the same treatment as discussed in Section 1.1. For the DMDHEU treatment the ASE of more than 50% was rather ineffective in preventing decay of sugi blocks by both decay fungi, whereas, for vapor phase formaldehyde treatment the ASEs of more than 50% and 20% were not necessary to suppress the decays by *T. palustris* and *C. versicolor*, respectively.

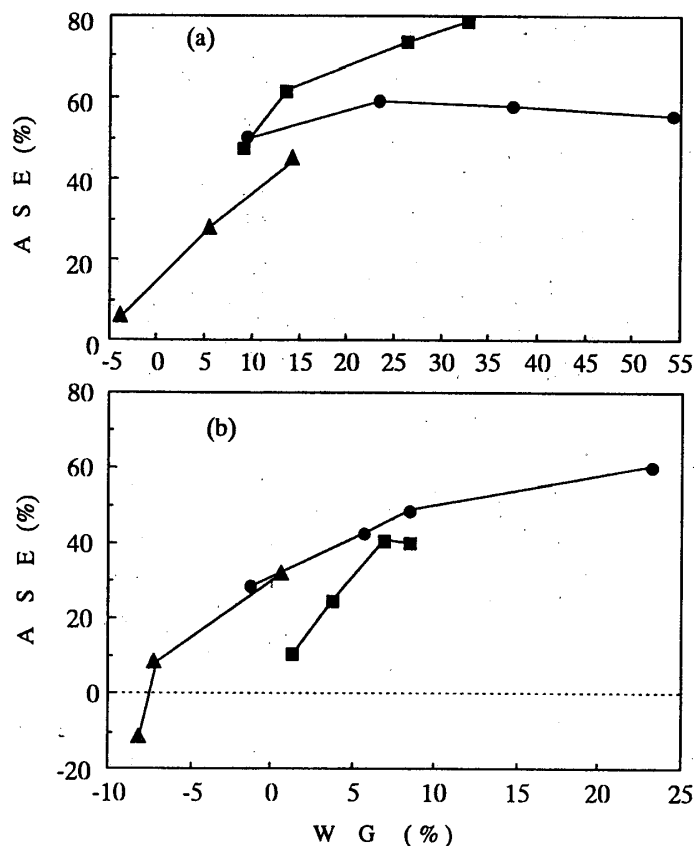


Fig 1.21. Relationship between weight gain and antiswelling efficiency (ASE) of treated sugi (a) and buna (b).

Legends: ■ Glutaraldehyd, ● : DMDHEU, and ▲ : Glyoxal.

Glyoxal treatment had a poor effect in preventing decay, although 15% WG and 45% ASE were obtained in sugi blocks treated with a 20% solution of this reagent (Figs. 1.19a and 1.21a). High values of WL were thoroughly observed when glyoxal-treated sugi was exposed to *T. palustris*, although WL reduced considerably when exposed to *C. versicolor*. It was often recognized that the effect of chemical modification on the decay resistance of wood varied with the fungus-wood combinations. The white-rot fungus *C. versicolor* was most susceptible to acetylation, while the brown-rotter *T. palustris* was most resistant to it, and the largest difference between the two occurred on the acetylated sugi¹⁴⁾. The difference of decay resistances between brown-rot and white-rot fungi also was found in formaldehyde-treated wood as described in Section 1.1 and the difference was thought to be caused by the preferential reactivity of lignin to the chemicals used, or to the differences of the decay-inhibiting effects due to the cellulolytic enzyme systems between the two fungi.

Among these three treatments, glutaraldehyde was ranked best in decay-inhibiting effect at the same WG levels. Furthermore, the treatment is superior to formalization, because the decay resistance of formalized buna wood was not so improved. As shown in Fig. 1.22a, the WL of buna drastically decreased at only 5% WG by the glutaraldehyde

treatment. DMDHEU was ranked after glutaraldehyde mainly due to its unsatisfied effect in preventing decay of beech by *T. palustris* (Fig. 1.22b). The decay-inhibiting effects for buna treated with formaldehyde in the vapor phase were always poorer than those of treated sugi. It is still unexplained why the decay-inhibiting effect of buna treated with any cross-linking reagents was lower than that of sugi except for glutaraldehyde. The inferior effects of this hardwood especially against *T. palustris* might be related to an insufficient distribution of the chemicals among the specimens, or their mild reactivity on the wood components and the strong action of the cellulolytic system of the brown-rot fungus.

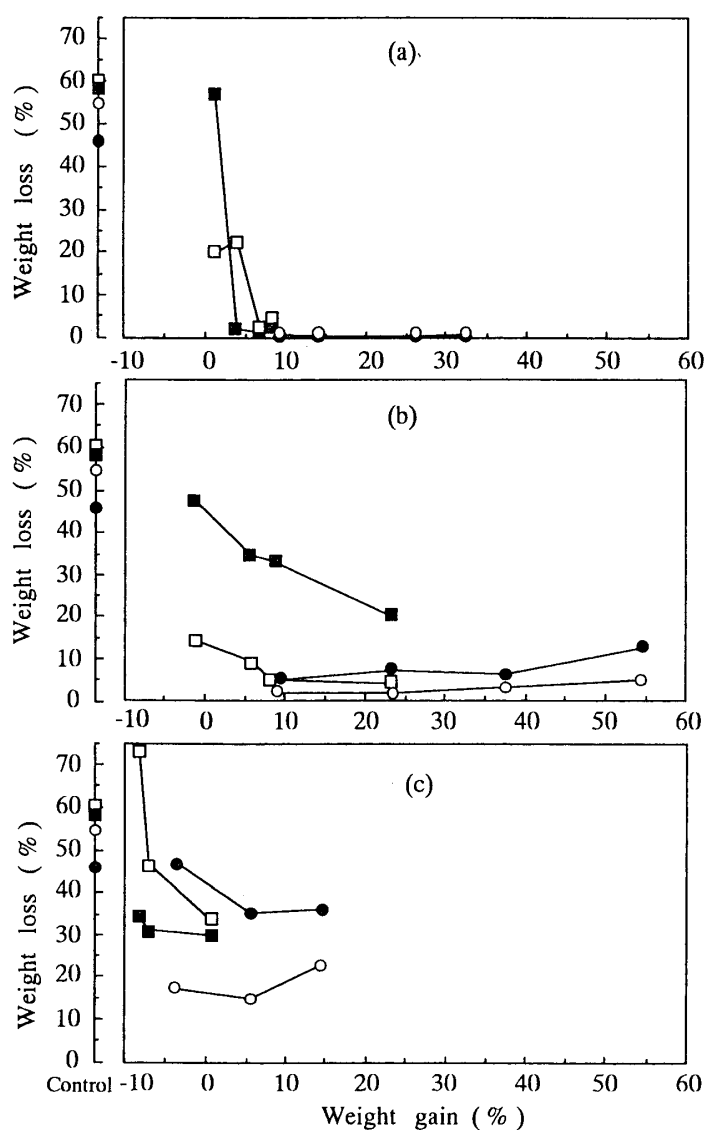


Fig 1.22. Average weight loss of glutaraldehyde- (a), DMDHUE-(b) and glyoxal- (c) treated wood after exposure to decay fungi for 12 weeks.

Legends: *Tyromyces palustris* (●: Sugi, ■: Buna)
Coriolus versicolor (○: Sugi, □: Buna)

Termite resistance

Weight loss (WL) and worker termite mortality (TM) are shown in Figs 1.23 and 1.24 for *C. formosanus* and *R. speratus*, respectively. Glutaraldehyde treatment of both wood species were most effective in preventing the attacks by the virulent termite, *C. formosanus*. WLs decreased to less than 5% in sugi and buna treated with the 10% solutions (Fig. 1.23a). While, WL reached less than 5% in DMDHEU-treated buna for the treatment with a 15% solution, but not in treated sugi at any concentration of the solution (Fig. 1.23b). Mortality of worker termites fed on sugi and buna blocks reached 100% when they were treated with 5% or 10% solutions of glutaraldehyde and DMDHEU.

In agreement with the resultant insufficient resistance against decay fungi, glyoxal-treated wood had poor resistance against *C. formosanus* too when it was evaluated for the WL

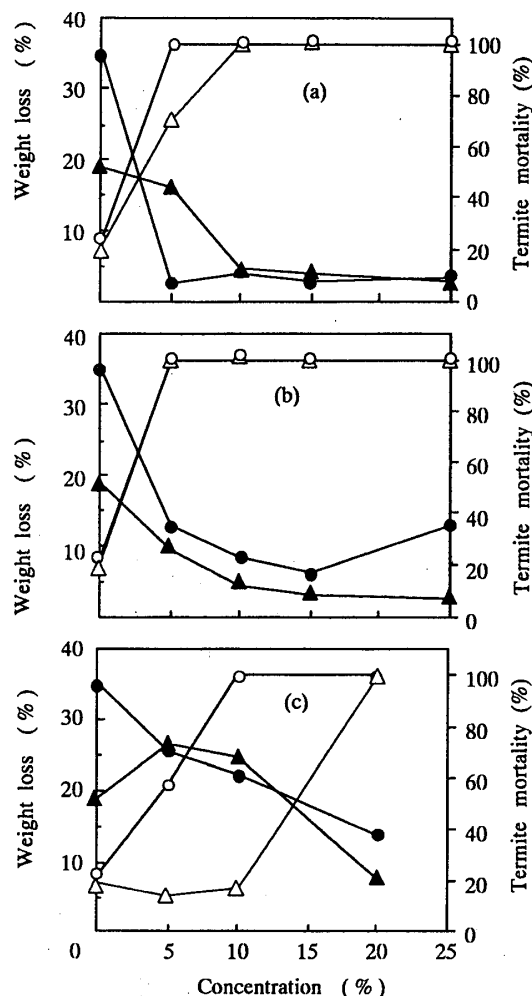


Fig 1.23. Average weight loss (WL) of glutaraldehyde-(a), DMDHEU-(b), and glyoxal-(c) treated wood and mortality (TM) of workers after exposure to termite of *Coptotermes formosanus* for 9 weeks.

Legend: ●, ○: WL and TM of sugi, ▲, △: WL and TM of buna.

of treated wood. However, TMs reached 100% in sugi and buna when treated with 10% and 20% solutions, respectively. In these cases, the mortalities of termites increased gradually consuming relatively large amounts of the target specimens, and reached 100% after 9 weeks. As observed in the forced-feeding tests of the wood treated with vaporous formaldehyde, the slow increase of mortality suggests that the termite resistance of the glyoxal-treated wood could not result from direct toxicity, but from some metabolic trouble due to a good deal of ingestion.

The effects of the treatments on the attack by *R. speratus* developed in a shorter period than that by *C. formosanus*, and the mortalities attained 100% within 3 weeks for all the treated specimens (Fig. 1.24). This probably resulted from the weak vitality of *R. speratus*, as often observed in the forced-feeding tests with chemically-modified wood as well as with

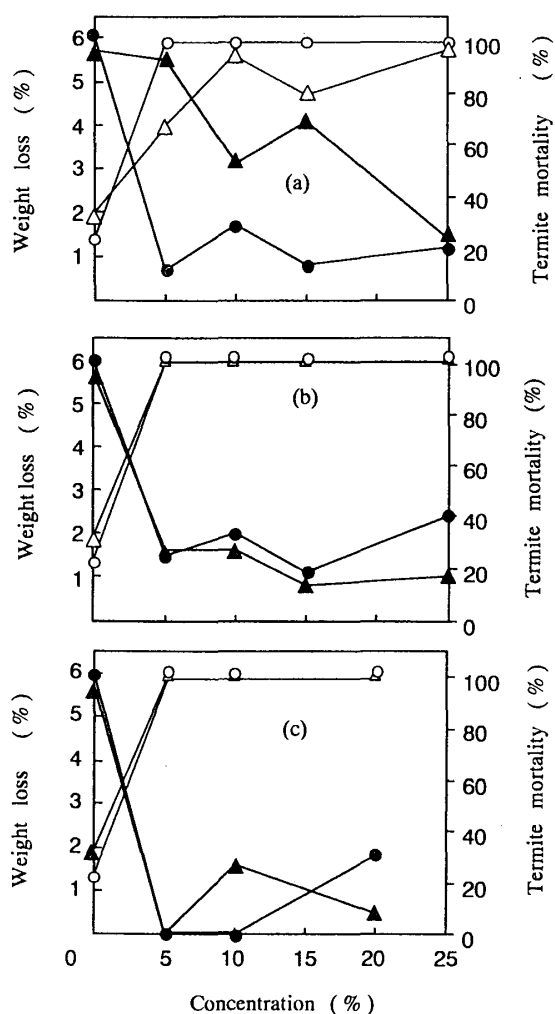


Fig 1.24. Average weight loss (WL) of glutaraldehyde-(a), DMDHEU-(b), and glyoxal-(c) treated wood and mortality (TM) of workers after exposure to termite of *Reticulitermes speratus* for 3 weeks.

Legend: See Fig. 1.23.

the wood treated with conventional toxic chemicals. The effect of the treatment was different between the two subterranean termites tested, and in the case of *R. speratus*, the glutaraldehyde treatment was ranked below other ones in comparison with WL and TM in treated buna blocks.

At the treatment level of vapor phase formalization providing the decay elimination, TMs of both termites reached 100% by the end of each test period but WL was still 10% for *C. formosanus*. Glutaraldehyde treatment was ranked higher than formalization in yielding lower WLs by *C. formosanus*. However, the treatment was not so effective against *R. speratus*.

As discussed in the previous chapter, formaldehyde-treated wood as well as acetylated wood could be eaten by the termites and taken into their intestines, but they were not digested in the termite body. As a result, the termites could not obtain any nutriment and forced to starvation. *C. formosanus* was more aggressive feeders than *R. speratus*, and the former was more resistant than the latter against starvation. The reason why this weak termite of *R. speratus* showed better endurance against glutaraldehyde-treated wood than the virulent termite of *C. formosanus* is not known yet.

1.3 Weathering Properties of the Wood Modified with Cross-Linking Reagents

1.3.1 Introduction

For outdoor uses of chemically modified wood, weathering properties such as change of color, occurrence of surface checks, and retention of high performance are considered to be important as are dimensional stability and biological resistance.

Feist and Hon³⁷⁾ classified the main factors responsible for natural weathering in wood as solar radiation, in particularly ultra violet (UV), moisture (rain, snow, dew, and so forth), temperature, and atmospheric gases. Among them, solar radiation is thought to be the most damaging factor for the wood cell wall components³⁸⁾ and then water which washes away degradation products causes the surface erosion.

Generally, the UV degradation process is triggered by the formation of free radicals, and probably it begins with the oxidation of phenolic hydroxyl groups in lignin³⁹⁾. Therefore, substitution of the phenolic hydroxyl groups of wood by other functional groups is expected to improve the resistance of wood against photo degradation.

Among the various chemical modification methods, acetylation was known to prevent discoloration^{40,41)} and cell wall erosion⁴²⁾ after natural weathering. Moreover, Kiguchi⁴³⁾ reported that esterification with butylene oxide could reduced photo deterioration. However, the effect of cross-linking formation, as in formalization, on the weathering properties has not been investigated yet.

In this section, the effects of the cross-linkings on weathering properties with and without surface coating and decay resistance after exposure to weathering conditions were examined.

1.3.2 Materials and Method

Cross-linking reagents

Four cross-linking reagents, tetraoxane as a source of formaldehyde, glutaraldehyde, glyoxal, and DMDHEU were used for chemical modifications. Among them, tetraoxane and DMDHEU were technical grade reagents, and glutaraldehyde and glyoxal were reagent grade ones.

Wood samples

Wood specimens, 50×100 (mm) in surface sizes and 2.5 mm in the thickness, were taken from sapwood veneer of radiata pine (*Pinus radiata* D. Don). They were subjected to chemical modifications with cross-linking reagents before exposure to weathering. After treatments, the veneers were glued with resorcinol resin and pressing at room temperature to form 2-ply laminated veneer. Two sets of treated specimens, with and without coating with film-forming transparent finishes, were prepared.

For the surface finishing, commercial type polyurethane resin type lacquer (Dainippon Toryo Co., Ltd.) was diluted with toluene and brushed twice at 100 g/m² for each coating, according to applicable recommendations provide by the manufacturer.

Treatments with cross-linking reagents

The procedure of formalization and the treatments with glyoxal, glutaraldehyde and DMDHEU were described in Sections 1.1 and 1.2, respectively.

All specimens treated were rinsed thoroughly in running water for several days to leach out un-reacted reagents from the specimens. The weight gains of the specimens were calculated from the oven-dried weights before and after treatment.

Weathering conditions

a) Natural weathering

Treated and untreated specimens of LVLs were exposed to the outdoor at an inclination of 45 degrees for 24 weeks from April to October 1993, on the campus of Kyoto University, Uji-City, Kyoto Prefecture, Japan.

b) Artificial weathering

An accelerated weathering was conducted artificially in a commercial chamber (Sunshine Super Long-life Weather meter WEL-SUN-HC, Suga Shikenki Co., Ltd.), in which weathering conditions of light-irradiation and water-spraying were combined. Specimens were exposed to a 3 kWh carbon-arc light as a UV source in an enclosed chamber at 50°C and 50% relative humidity. Distilled water was sprayed on specimens for 12 minutes every one hour. Exposure times ranged from 0 to 720 hrs.

Determination of color differences

The color change was determined at three locations on the surfaces of each specimen by using a Color and Color Difference meter (Z-1001DP, Nippon Denshoku Kogyo Co., Ltd. for natural weathering, and a TOP-scan TC-1800MK-II, Tokyo Denshoku Co., Ltd. for

artificial weathering). The average color difference (ΔE^* s) was calculated from the values of L^* , a^* , and b^* at each location on the samples before and after weathering.

Visual inspection of checking

The extent of surface checking after artificial weathering was inspected visually for 120 to 720 hrs by ratings as follows:

- 0—No sign of checking.
- 1—Checking occurred on less than 10% of surface area.
- 2—Checking occurred on 10%–20% of surface area.
- 3—Checking occurred on 20%–40% of surface area.
- 4—Checking occurred on 40%–60% of surface area.
- 5—Checking occurred on more than 60% of surface area.

In this case, the surfaces of each specimen were sectioned into one centimeter squares, and the numbers of squares with more than one check were counted to calculate the proportion of the total number of squares. In addition, the weight of each specimen after exposure to the artificial weathering was measured to calculate the weight loss.

Observations by scanning electron microscope (SEM)

SEM observation procedure was described in Section 1.1.

Evaluation of the decay resistance before and after weathering

Before and after the specimens were exposed to artificial and natural weathering, they were subjected to the fungal decay test according to the JWSA Standard No.3-1992. These procedures have been already described in Section 1.1.

1.3.3 Results and Discussion

Color changes and weight gains after treatments

The specimens became brown to dark brown after treatments. Of these treatments, the glutaraldehyde treatment resulted in darker than the others.

Average WGs after treatments are shown in Table 1.4. In 24 hrs, DMDHEU, glutaraldehyde and glyoxal treatments gave considerably large WGs when compared to the vapor-phase formalization. At high levels of WGs attained in this experiment, more than 60% of ASE was gained.

Table 1.4. Average values of WG of radiata pine specimens after treatments with cross-linking reagents.

Reagents	Treatment	Reaction Time (hr)	WG (%)
Tetraoxane	Vapor phase	24	3.6
DMDHEU	Pad-dry-cure	24	24.9
Glutaraldehyde	Pad-dry-cure	24	21.1
Glyoxal	Pad-dry-cure	24	17.4

Color stability

Natural weathering changed the surface color to gray with accompanying roughness and pollution, and artificial weathering caused a lost of brightness, and discolored the surfaces of the untreated and treated specimens especially when unfinished. The surface films coated by the finishing were broken and removed almost from the surfaces of all specimens after natural and artificial weatherings, and they were detached first from the glyoxal-treated specimens. The growth of mildew was observed partially on unfinished and finished specimens when any chemical treatments were not introduced.

Relationships between color differences (ΔE^* s) of wood specimens and exposure times during natural and artificial weathering periods are shown in Figs. 1.25 to 1.28. In the natural weathering test of the LVL (Figs. 1.25 and 1.26), coating films could not affect the color difference of all specimens, but ΔE^* s of treated specimens were less than those of untreated controls. DMDHEU-treated specimens gave smaller and glutaraldehyde-treated ones gave larger ΔE^* s than did formaldehyde-treated ones. Incidentally, all specimens, especially treated ones, had rapid increases of ΔE^* s in the early stages of weathering and constant levels in the later stage. Therefore, the changes of colors due to weathering effects might go on in the early stages of UV irradiation. After long-term exposure to natural weathering, dust, chemical pollutant, and sand, as well as mildew, should be adhered to the wood surfaces, and these contaminations might be accelerated for untreated wood, resulting in surface colors with gray to dark-gray appearances.

Figures 1.27 and 1.28 show the relationships of ΔE^* s of radiata pine LVLs versus

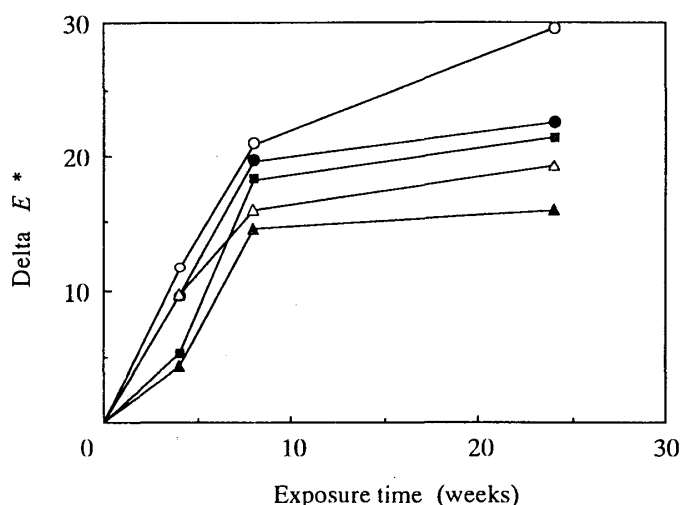


Fig 1.25. Color difference of unfinished LCVLs treated with cross-linking agents after outdoor exposure for 24 weeks.

Legend: ○: Control, ●: Glutaraldehyde, ■: Tetraoxane, △: Glyoxal, ▲: DMDHEU.

Note: Average values of 4 replicates.

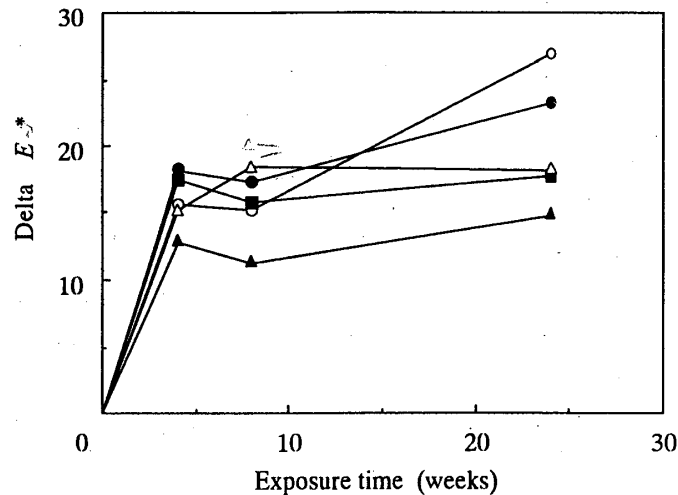


Fig 1.26. Color difference of finished LVLs treated with cross-linking reagents after outdoor exposure for 24 weeks.
Note and Legend: See Fig. 1.25.

exposure times in artificial weathering. In finished specimens without any treatments, ΔE^* s increased rapidly within the first 120 hrs and then reached to 20, while ΔE^* s of all treated specimens were less than 10 even after 720 hrs of weathering.

On the contrary, all unfinished specimens showed different relationships between color differences and exposure times. Delta E^* s increased somewhat constantly with time until 480 hrs; furthermore, all treated specimens yielded greater ΔE^* s than the untreated controls. Without the addition of a film coating on the surface of wood, easy degradation and leaching of the lignin would be caused by UV light irradiation and water spray showing the bleached appearance. Delta E^* s of unfinished specimens increased more, even in the

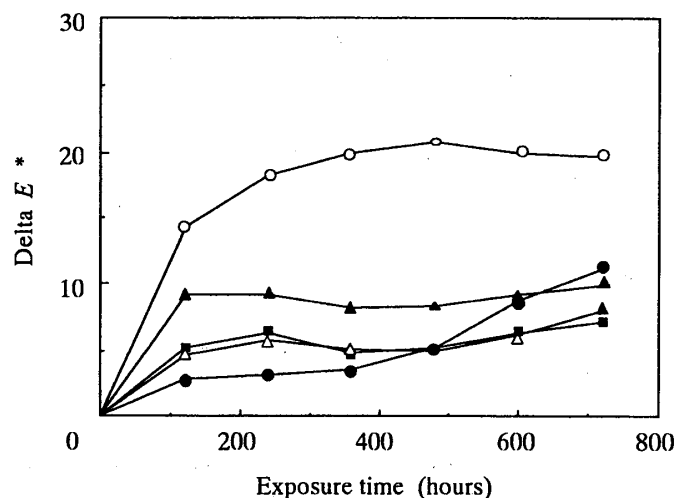


Fig 1.27. Color difference of finished LVLs treated with cross-linking reagents after artificial exposure for 720 hrs.
Note and Legend: See Fig. 1.25.

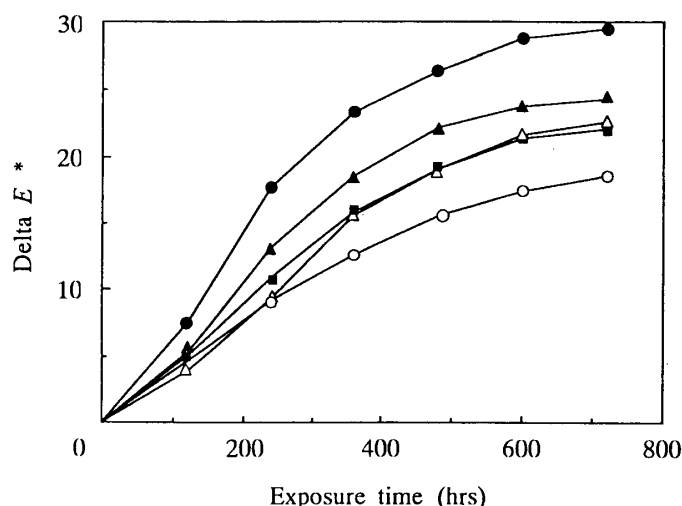


Fig 1.28. Color difference of finished LVLs treated with cross-linking reagents after artificial exposure for 720 hrs.
Note and Legends: See Fig. 3.1.

treated specimens.

Airborne particulates, which would cause the contamination of wood in the case of natural weathering, were considered not to be responsible in artificial weathering. Thus, the surfaces of the treated specimens, which were originally provided with dark color, should be affected by the bleaching effects more than untreated ones. Of the four agents, glutaraldehyde always gave the largest ΔE^* s.

Checking after weathering

Surface checkings of untreated and treated specimens during artificial weathering and their average weight losses after 720 hrs are shown in Table 1.5. All treatments were effective in retarding checking, irrespective of the finishing. Effectiveness of finishing in reducing surface checkings was obviously seen in both treated and untreated specimens.

According to Feist *et al.*⁴⁴⁾, film-forming finishes performed equally well on acetylated and untreated fiberboards after two years of outdoor exposures. On the other hand, a penetrating semitransparent oil-based stain did not performed as well on acetylated fiberboard because the finishes could not penetrate the treated surface. They concluded that therefore not as much material could be applied to the acetylated boards. The film-coating finish conducted in this experiment reduced the surface checkings; however, it could not affect the color stability after natural weathering. In agreement with their description, types of finishes which can give the best performances should be investigated for cross-linking modified wood.

Weight losses of control specimens after weathering were smaller than those of treated specimens. The values of WLs were largest in glyoxal-treated specimens, but DMDHEU- and glutaraldehyde-treated ones also lost fairly large amounts of weight by exposure to

weathering. Weight loss of untreated specimens after weathering might be due to the loss of lignin and organic solvent extractives by photo degradation. The degradation of the cell wall substances should be added to the values of WLs by leaching effects of water sprays.

The formaldehyde treatment has been considered as causing some reductions of the mechanical properties, and as a result it might be accelerated by the treatment when the exposed surfaces are degraded and new layers of wood are exposed progressively on the top surface of the sample. This would be coincidental with the relatively large values of WLs of the treated woods, and also the surface appearances by SEM as discussed below. Larger WLs of treated specimens, especially observed in glyoxal- and DMDHEU-treated specimens, were considered to be caused by the addition of the loss of the chemical reagents which would be leached away by weathering. The chemical compounds which had been impregnated and remained in the cell lumina and the cell walls after the curing and leaching procedure of the experiment, should be eroded by photo irradiation and the washing effects of water spray.

Table 1.5. Rating of surface checking in LVLs during artificial weathering and their weight loss after 720 hrs.

Reagents of treatments	Surface coating	Rate of checking								Weight loss
		Time of weathering (hrs)								
		0	120	240	360	480	600	720	(%)	
Control	Yes	0	0	0	0	0.3	1.0	1.0	3.7	
	No	0	0.2	0.3	1.0	2.2	2.2	2.2	4.8	
Tetraoxane	Yes	0	0	0	0	0.3	0.5	0.7	5.5	
	No	0	0	0	1.2	1.4	1.5	1.6	4.8	
DMDHEU	Yes	0	0	0	0	0.1	0.2	0.5	6.2	
	No	0	0	0	0.1	1.5	1.6	1.7	10.4	
Glutaraldehyde	Yes	0	0	0	0	0	0.2	0.5	6.2	
	No	0	0	1.0	1.5	1.5	1.5	1.5	9.7	
Glyoxal	Yes	0	0	0	0	0.5	0.5	0.5	22.8	
	No	0	0	0	1.0	1.0	1.0	1.0	26.5	

Note: Average values of 4 specimens.

SEM observation

Figures 1.29 and 1.30 show the low-magnification pictures of the surfaces of untreated and treated specimens after 720 hrs exposure of artificial weathering. In the untreated veneer, many large checkings are seen over the entire surfaces, whereas checks are observed to be small and narrow on the treated specimens and to be scattered.

Weathering led to the early disintegrations and enlargements of bordered pits, extensive separations of the late wood tracheid walls in the middle lamella and minute checks oriented

along the microfibrils of the S_2 layer in the cell walls⁴⁵⁾. These characteristic patterns of cell wall erosion due to weathering were essentially the same in both untreated and treated woods.

SEM observations visualized the formation of the large surface checks along the fiber lengths in the untreated specimens, but checks were dispersed over the surfaces with small sizes in the treated ones. In the treated wood provided with dimensional stabilization, the occurrence of extensive microscopic and macroscopic checks could be limited which should lead to distortions of the cell alignment.

However, the surface appearance was observed to be somewhat fragile or brittle for the formaldehyde-treated specimens. Although SO_2 was introduced as the catalyst of the cross-linking reagents to reduce the strength loss of the treated wood, some decrease of mechanical strength was inevitable in the treatment process because of high temperature conditions up to 120°C .

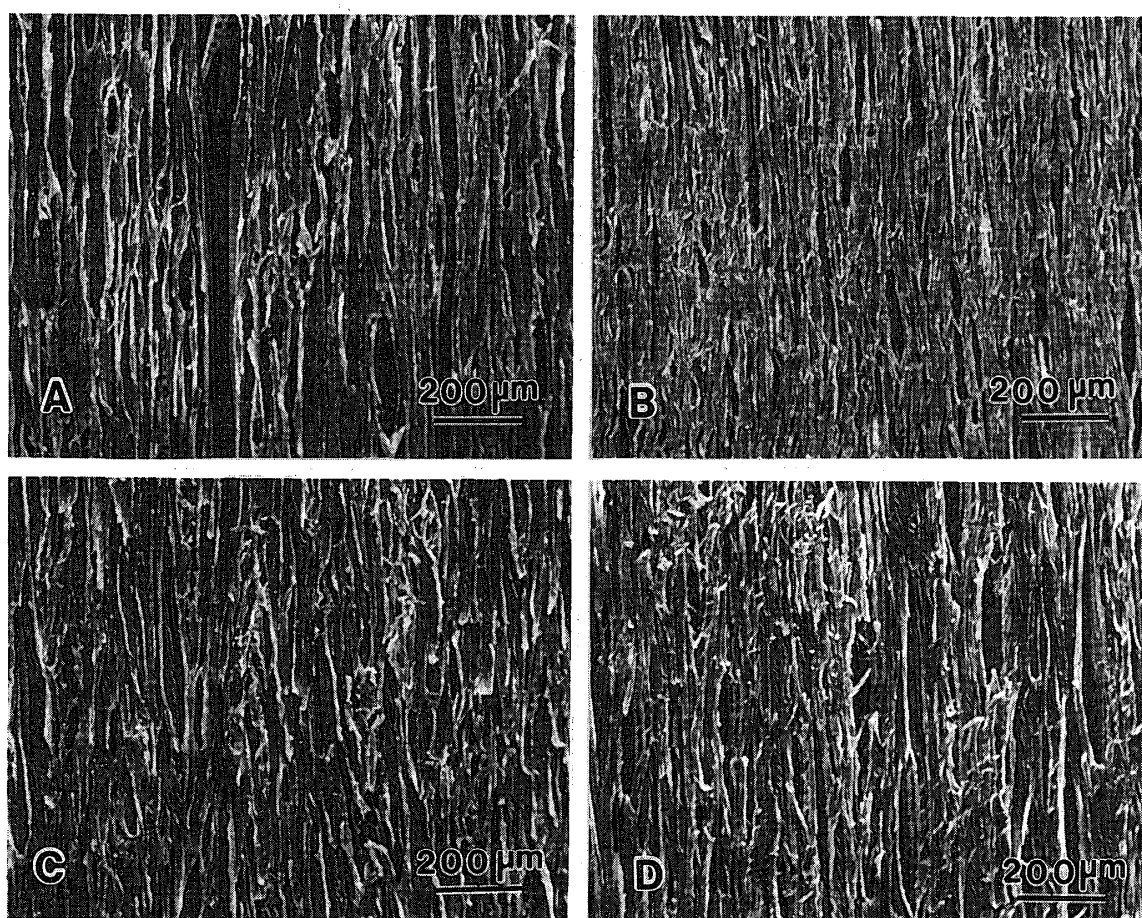


Fig 1.29. SEM observations of the unfinished surface of untreated (A), tetraoxane (B), DMDHEU (C) and glutaraldehyde (D) treated LVLs after exposure to artificial weathering for 720 hrs.



Fig 1.30. Formaldehyde-treated LVL after exposure to artificial weathering for 720 hrs, showing diagonal fissures following the microfibril angle of the S_2 layers.

Decay resistance after weathering

The WLs of untreated and treated samples obtained from decay tests before and after weatherings are shown in Table 1.6. This table indicates that before weathering WLs of untreated specimens were about 25% and 21% for unfinished and finished samples, respectively. However, WLs drastically decreased after treatments with the cross-linking reagents, especially with formaldehyde and/or glutaraldehyde. Weight losses of the samples treated with DMDHEU were relatively more than the above two cross-linking reagents, although the WLs could be suppressed to about 80% of the untreated ones. Glyoxal treatment had a poor effect in preventing decay, and the same results also were observed in Section 1.2. The WLs of finished samples were relatively smaller than those of unfinished samples for both untreated and treated specimens, and this probably was due to the effectiveness of film coating which might physically have reduced the developments of fungal mycelia onto and into the wood substances.

Judging from the values of WLs, decay resistances of untreated and treated samples were observed to be decreased somewhat after the artificial and natural weatherings. Among them, formaldehyde- and DMDHEU-treated woods still were efficient in preventing decay attacks even after exposures to artificial weathering for 720 hrs and natural weathering for 24 weeks. It was probably due to the fact that photo irradiation could not break the cross-link bridges between the OH-bonds of wood components and these reagents.

Table 1.6. Weight loss of untreated and treated specimens caused by decay test for 8 weeks before and after weathering.

Exposure condition and cross-linking reagents	Unfinished		Finished	
	TYP	COV	TYP	COV
Before weathering				
Untreated	25.0	24.7	21.8	21.6
Tetraoxane	0.6	0.4	0.4	0.2
DMDHEU	5.2	4.2	3.0	2.4
Glutaraldehyde	1.7	1.1	1.5	0.8
Glyoxal	21.7	16.5	21.3	16.0
After artificial weathering				
Untreated	29.1	28.2	33.2	25.4
Tetraoxane	2.7	2.1	1.8	1.5
DMDHEU	8.7	1.7	7.0	1.6
Glutaraldehyde	14.4	3.9	10.3	2.6
Glyoxal	22.6	17.8	22.3	11.4
After natural weathering				
Untreated	26.8	25.7	25.2	21.9
Tetraoxane	2.5	0.5	1.8	0.3
DMDHEU	7.3	3.5	5.7	2.1
Glutaraldehyde	8.5	2.8	8.1	2.6
Glyoxal	18.9	10.4	17.8	9.6

Legends: TYP: *Tyromyces palustris*, COV: *Coriolus versicolor*.

Note: Average values of 9 specimens.

However, the glutaraldehyde-treated samples, which had been provided with decay-inhibiting effects before weathering, drastically lost decay resistances after exposure to weathering, especially artificial weathering. It is considered that the bulking or cross-linking effects with glutaraldehyde should be eroded when exposed to photo irradiation, although they provided great resistance to decay before weathering.

Chapter 2 Application of Cross-Linking Formation to the Reconstituted Wood Products

2.1 Properties Enhancement of Laminated Veneer Lumber (LVL) Modified with Some Cross-Linking Reagents

2.1.1 Introduction

Despite extensive research on the dimensional stability of chemically modified solid wood, little effort has been made to apply chemical modification to reconstituted wood products, such as laminated veneer lumber (LVL), waferboard, fiberboard, and so on. For efficient utilization of lesser-used wood species or small-diameter and low-grade logs, the

production of reconstituted wood products is expected to be a potential means and increase because of their enhanced physical and mechanical properties as well as the global circumstances of forest resources.

However, only the superiority of mechanical properties, and economical and ecological affairs of these products is not enough, when they are exposed to biological and weathering hazards. It is necessary to provide these products with some other high-performance particularly in enhancing the biological resistance and dimensional stability by additional treatments such as chemical modification.

In this section, dimensional stability and biological resistance were evaluated on Douglas fir LVLs modified with some cross-linking reagents. Veneer of Douglas fir were chemically modified by vapor phase formalization or pad-dry-cure treatments with the non-formaldehyde cross-linking reagents prior to the production of LVLs.

2.1.2 Materials and Method

Wood samples

Wood specimens with the size of 50×100 (mm) were taken from 3.0 mm thick rotary veneer of Douglas fir (*Pseudotsuga menziesii* Franco) sapwood. They were subjected to chemical modifications before pressing into LVLs.

Treatments with cross-linking reagents

The vapor-phase formalization and pad-dry-cure treatments were described in Sections 1.1 and 1.2, respectively.

LVLs production

The untreated and treated Douglas fir veneers were pressed (5 kg/cm² and thickness 13 mm) into 5-ply LVLs, under room temperature for 24 hrs using resorcinol resin as a binder at about 200 g/m². Five treated and untreated LVLs were produced and subjected to testing of physical properties and biological resistance.

Water swelling test

For evaluation of the thickness swelling (TS) on radial direction and linear expansion (LE) on tangential direction of three replications for untreated and treated LVLs, they were placed in water bath with a controlled temperature. The specimens with 20 mm square were soaked in water at a room temperature for 1 day under the reduced pressure. Then they were kept in hot water at 70°C for 2 hrs, and boiling water for 2 hrs. Dimensions of the test specimens were measured immediately after taking out from water bath on each step to evaluate the changes of TS and LE.

Changes of TS and LE for untreated and treated LVLs were also determined during the 4-cycle accelerated aging test. The specimens with 50 mm square were soaked in water for 4 days and then dried in an oven for 3 days at 60°C, and these cyclic conditions were continued 4 times.

Decay and termite tests

These measurements were already described in Section 1.1.

2.1.3 Results and Discussion

Weight gain (WG)

The average values of WGs of veneers for LVLs after the treatments with the cross-linking reagents are shown in Table 2.1. The WG was highest in DMDHEU, and followed by glutaraldehyde and formaldehyde. The WG values were increasing with increases of the concentration of the solutions on both pad-dry-cure treatments, and reached about nearly 9% at the highest concentration of DMDHEU. This would mean that the dimensional stabilization due to these reagents might be attributed to the bulking effect to some extent, even though the cross-linking should exist as suggested by Yasuda *et al.*³⁶⁾.

Table 2.1. WG of veneer treatment with cross-linking reagents.

Reagents	Levels	WG (%)
(Formalization)	(React. time)	
Tetraoxane	5 hr	0.8
Tetraoxane	10 hr	1.0
Tetraoxane	24 hr	1.2
(Pad-dry-cure)	(Conc.)	
Glutaraldehyde	2.5%	1.4
Glutaraldehyde	5 %	4.7
Glutaraldehyde	10 %	7.2
DMDHEU	2.5%	−0.5
DMDHEU	5 %	5.6
DMDHEU	10 %	8.6

Biological resistance

The WLs of untreated and treated LVLs after 12 week exposure to the brown-rot fungus, *T. palustris*, and the white-rot fungus, *C. versicolor*, are shown in Fig. 2.1. The WLs of untreated LVLs after exposure to *T. palustris* and *C. versicolor* were about 40% and 29%, respectively.

The LVLs treated with vapor phase formalization for 0.8% of WG showed the relatively small WLs of 2.2 and 3.4% after exposure to *T. palustris* and *C. versicolor*, respectively. The average values of WLs decreased with increases of WG for treated LVLs, and almost complete elimination of decay was attained after 24 hrs of reaction time (1.2% of WG). However, as will be described in the following chapter, the WLs of treated albizzia waferboards were nil even at 5 hrs of reaction time, and 12 hrs of reaction time was required

for solid wood blocks of sugi with the small dimensions as discussed in Section 1-1. The penetration and the reactivity of the gaseous formaldehyde to the specimens affect of this cross-linking reagent with wood substances.

In the pad-dry-cure treatment, the glutaraldehyde- and DMDHEU-treated LVLs also showed the relatively small WLs in all levels of the chemical concentrations. The DMDHEU- and glutaraldehyde-treated LVLs needed higher WGs than the vapor phase formalization to eliminate the decay attack by both fungi. This suggests that the bulking due to the impregnation of these two agents played the major role in the effect.

It has been pointed out that the unreacted reagents remained in wood specimens after these treatments might show some toxic effects on the wood attacking micro-organisms.

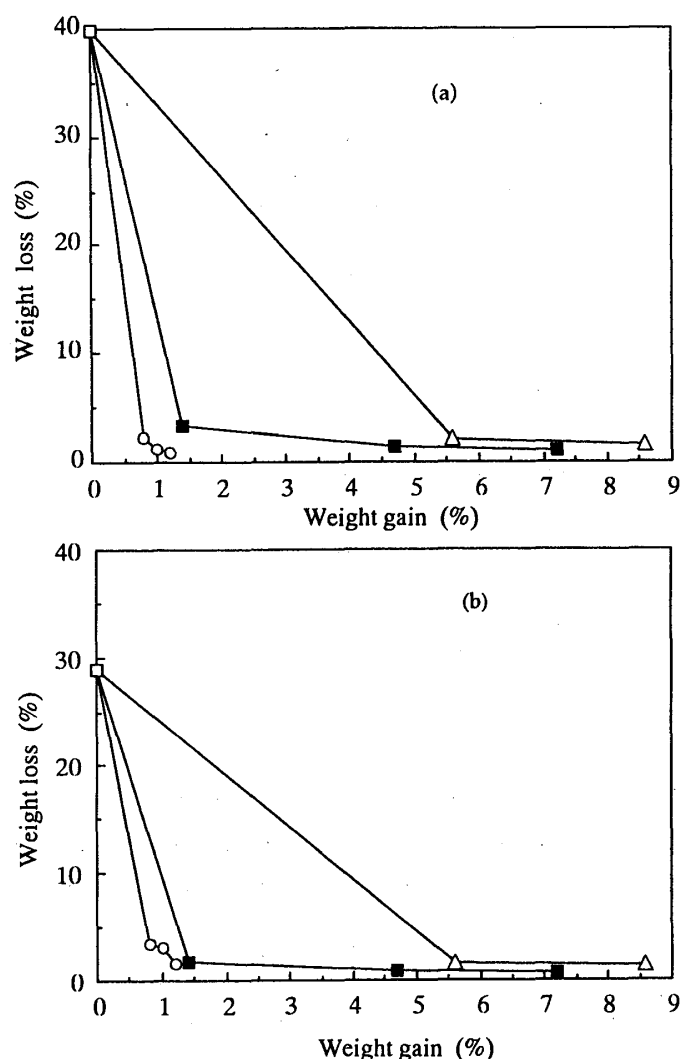


Fig. 2.1. The WL of LVLs treated with cross-linking reagent after 12 weeks exposure to *Tyromyces palustris* (a) and *Coriolus versicolor* (b).
Legend: ○: Formaldehyde, ■: glutaraldehyde, △: DMDHEU, □: Untreated.

However, in the present process, the treated samples were evacuated at 120°C for 6 hr for vapor phase formalization, and rinsed in running water for pad-dry-cure treatment to eliminate the residues of the reaction chemicals. According to Dewispelaere *et al.*⁴⁾, the over-growing of fungal mycelium on the treated wood blocks suggests the non toxicity of reagent, therefore the over-growing on treated LVLs observed in this experiment showed the absence of toxic effect in them.

Incidentally, the adhesives used in the manufacture of reconstituted wood products are of great importance for the fungal growth, because urea-melamine and isocyanate resins can have a promoting effect, and phenolic resins an impeding effect. It has been reported that unleached particleboards glued with phenol resin showed some toxicity to a brown-rot fungus in soil block decay tests¹⁴⁾. The presence of some water soluble toxic materials in the resorcinol resin used in this experiment might inhibit or slow down the attack by *T. palustris*.

The WLs of the untreated and treated LVLs after the forced-feeding test by termites of *C. formosanus* are shown in Fig. 2.2. The average value of WLs of untreated LVLs was about 17% after termite exposure for 9 weeks, but those of treated LVLs were below 7%. The WLs did not decreased remarkably with increases of the reaction times for vapor phase formalization and the concentrations for pad-dry-cure treatments, and the effectivenesses of these treatments in restricting the termite attack were not as sufficient as was decay resistance. Nevertheless, 100% TM was achieved by the low level of treatment within the test period of 9 weeks, whereas mortality of termites fed on untreated LVLs was below 20% at the end of the tests.

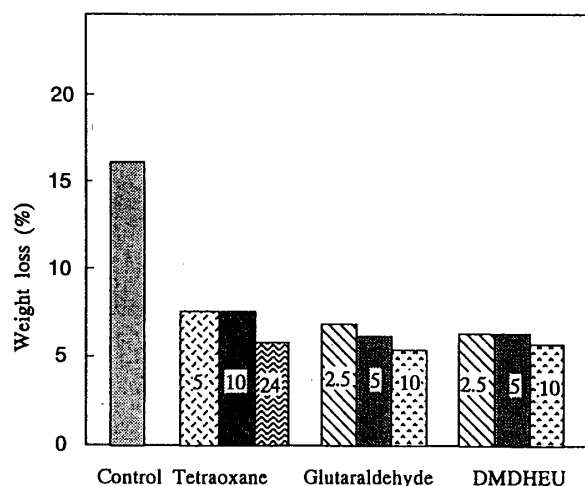


Fig. 2.2. The weight loss of cross-linking agents-treated veneer of LVLs after exposed to termite attack of *Coptotermes formosanus* for 9 weeks.

Note: The number in the figure shows percent incorporated concentration.

Physical properties

When LVLs are used for structural members exposed to high humidity conditions or rain fall, they should be suffered from the dimensional change or the occurrence of cracks. Such defects have restrained LVLs from the structural use, so that the high level stabilization on thickness swelling and linear expansion along tangential direction would expand the new utilization of LVLs.

The TS in radial direction and the LE in tangential direction of specimens after water soaking at room temperature and soaking in hot and boiling water are shown in Figs. 2.3 to 2.5.

Values of TS of treated LVLs after soaking in water were definitely smaller than untreated LVLs, especially after soaking in boiling water. Those of untreated LVLs were about 5% after room temperature water immersion, and 6% and 7% in hot water soaking and boiling, respectively. However, the TS values measured after each step of water

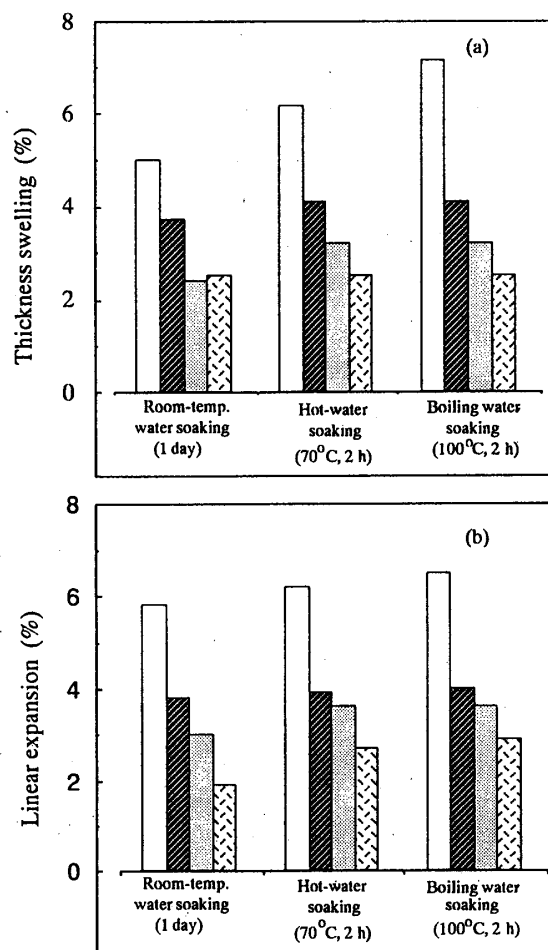


Fig. 2.3. Thickness swelling (a) and linear expansion (b) of formaldehyde-treated LVLs after water immersion.

Legend: □: Untreated, ▨: treated for 5h, ▩: 10h, and ◻: 24h.

swelling test decreased with increases of the reaction time for formalization, and the solution concentrations for pad-dry-cure treatment. All treated LVLs exhibited very small TS values below 3% even after boiling in water.

This should be due to the reduction of hygroscopicity of wood components because of the cross-linking formation in hydroxyl groups and/or bulking in the wood cell walls. These results also indicated that the cross-linking formation by both treatments and the bulking by pad-dry-cure treatments were stable even after boiling in water for 2 hrs, and that the treatments were very effective in reducing the thickness swelling and linear expansion of LVLs.

The values of LE decreased with increases of the reaction time for formalization, and the solution concentrations for pad-dry-cure treatment. All treated LVLs exhibited very small LE values below 3% for formalization and DMDHEU treatment, and of about 4% for

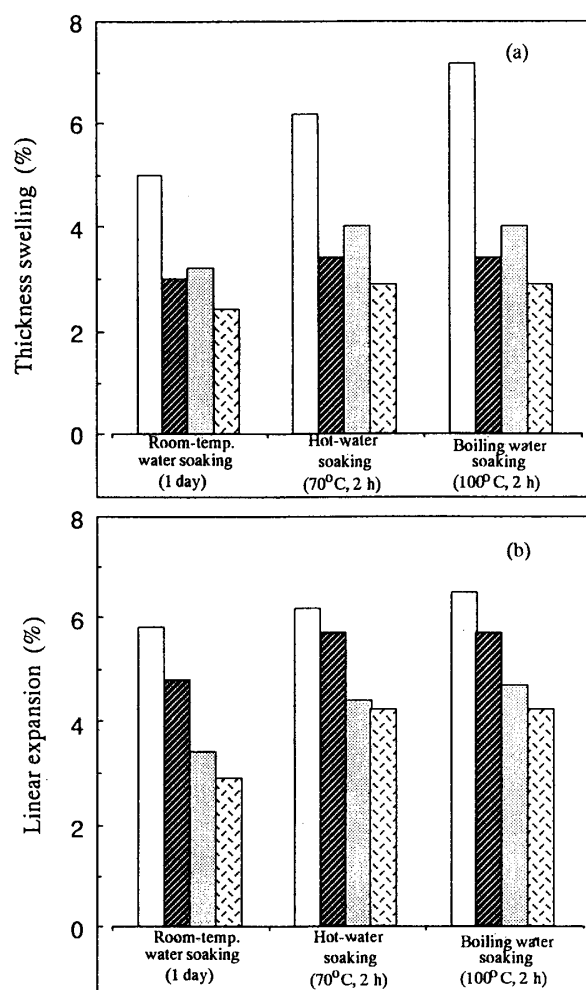


Fig. 2.4. Thickness swelling (a) and linear expansion (b) of glutaraldehyde-treated LVLs after water immersion.

Legen: See Fig. 2.3.

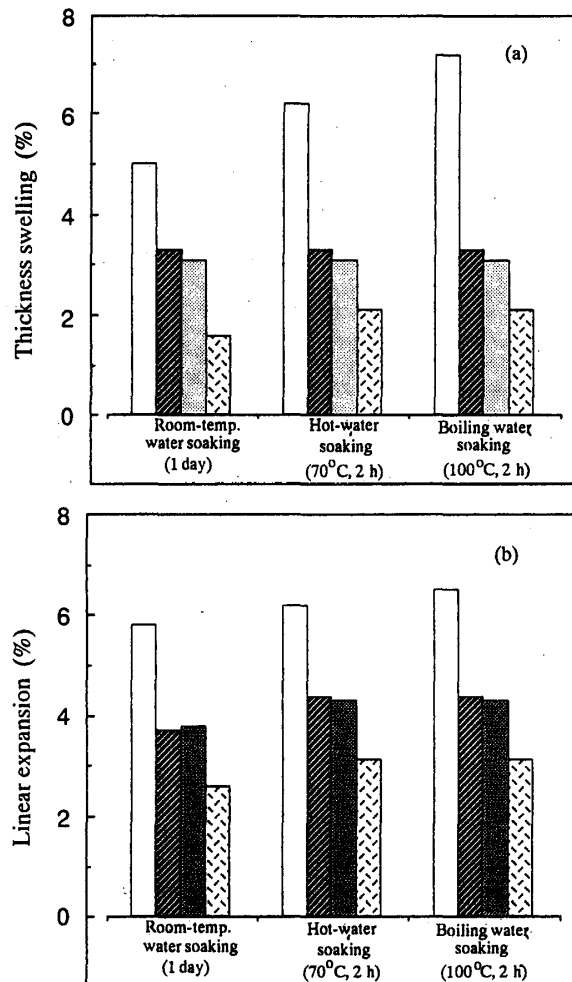


Fig. 2.5. Thickness swelling (a) and linear expansion (b) of DMDHEU-treated LVLs after water immersion.
Legend: See Fig. 2.3.

glutaraldehyde treatment even after boiling in water.

The changes of TS and LE of untreated and treated LVLs after 4 cycles of the water soaking-drying tests at room-temperature are shown in Figs. 2.6 and 2.7. Resoaking of untreated LVLs in water caused additional irreversible stresses to be relieved and greater thickness swelling was observed than during the first soaking cycle (Fig. 2.6). These dimensional changes were also detected for the LVLs with low level treatments. However, treated LVLs at the highest levels of reaction time for formalization and the solution concentration for pad-dry-cure underwent much less swelling through the water soaking-drying cycles.

Additional increases of LE for untreated LVLs and its prevention for treated LVLs during water soaking-drying cycles was hardly detected, but the dimensional changes were evidently suppressed by the application of these chemical modifications (Fig. 2.7).

No delamination of veneers along the glue line was visually detected for untreated and treated LVLs after boiling.

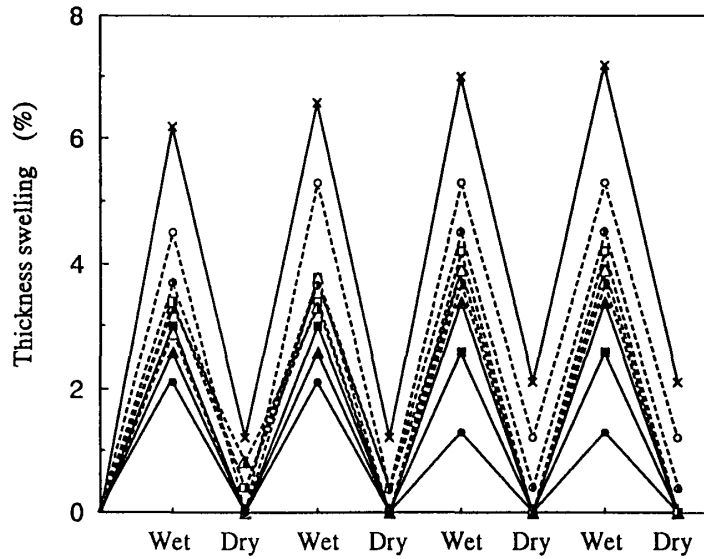


Fig. 2.6. Thickness swelling of untreated and treated LVLs after 4-cycle dry and wet aging test.

Legend: X : Untreated, ○ : treated with formaldehyde for 5hr, ○ : 10hr and ● : 24hr, △ : treated with glutaraldehyde 2.5%, △ : 5%, and ▲ : 10%, □ : treated with DMDHEU 2.5%, □ : 5%, and ■ : 10%.

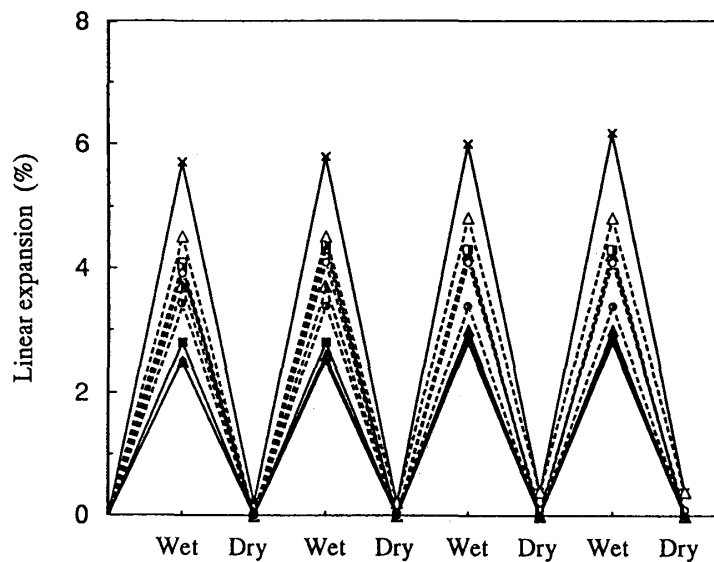


Fig. 2.7. Linear expansion of untreated and treated LVLs after 4-cycle dry and wet aging test.

Legend: See Fig. 4.6.

2.2 Dimensional Stability and Biological Resistance of Waferboard Treated with Cross-Linking Reagents

2.2.1 Introduction

Albizzia (*Paraserienthes falcata* Becker) is a fast growing tree planted in tropical countries, especially in South East Asia, but it is not utilized for a building material because of its perishability and poor mechanical properties. To expand the utilization of these lesser-used wood species, the production of reconstituted wood products such as waferboard, particleboard, and medium-density fiberboard (MDF) are assumed to be a potential means.

However, only the superiority of mechanical and aesthetically properties of these reconstituted wood products is not enough, when they are used in wet-tropic regions where they are exposed to biological and weathering hazards. It certainly is necessary to provide these products some other high performance particularly in enhancing the biological resistance and dimensional stability by additional treatment such as chemical modifications. Greater biological resistance and dimensional stability have been achieved by acetylation of albizzia particleboards^{20,46)}, and it was also reported that the physical and biological properties of MDFs were greatly improved by vapor phase formalization⁴⁷⁾.

In this chapter, physical and biological properties of albizzia waferboards modified with cross-linking reagents were described. The vapor phase formalization was applied after the board production, and the pad-dry-cure treatments with other reagents were made prior to the board processing.

2.2.2 Materials and Methods

Wafer preparation

The raw materials were prepared from logs of albizzia having an air-dry density of 0.3 g/cm³. The logs were cut from trees that were growing in Indonesia for ten years. Wafers were prepared using a disc-flaker, with the average dimensions of 30 mm in width and length, and 0.4–0.8 mm in thickness.

Formalization of waferboard

The vapor phase formalization was applied to waferboards using tetraoxane as a vapor source of formaldehyde and sulfur dioxide as a catalyst. Specimens for treatment were cut from waferboards with the sizes corresponding to each testing method and procedure of formalization was described in Section 1.1.

For pad-dry-cure treatment, the wafers were impregnated with 5% and 10% of reagent-grade glutaraldehyde and commercial-grade DMDHEU for 4–7 days until they sank to the bottom, and then were dried in the room temperature for one week. The impregnated wafers were put in the glass vessel and curing was conducted in an oven for 24 hr at 120°C as described in Section 1.2.

Waferboard production from chemically modified wafers

The wafers were pressed into low-density waferboards using isocyanate (UL-4800)

resin, formulated by Gun-ei Kagaku Co., Ltd. as a binder. After the moisture content of wafer was adjusted at 11%, the resin was sprayed onto the wafers to yield 8% solid content of resin based on the oven-dry weight of wafers. Wafer mats formed by hands were pressed at 160°C for 5 minutes into the boards with the target density of 0.4 g/cm³ in air-dry condition and with the dimensions of 200×200×10 mm.

Water swelling test

To determine the values of ASE, the specimens were soaked in water at room temperature for 3 days, and then the thickness changes were measured. For evaluation of the thickness swelling and linear expansion of the specimens, they were placed in water bath in which temperature could be controlled. The specimens were soaked in water at room temperature for 1 day under the reduced pressure. Then, they were kept in to water for 2 hr at 70°C, and boiling water for 2 hr. Dimensions of the test specimens were measured immediately after taking from each water bath to evaluate the changes of the TS and the LE. Change in thickness swelling of the boards were also determined during the 4 cycle accelerated aging test which consisted of soaking in water for 4 days and then drying in an oven for 3 days at 60°C.

Mechanical strength tests

Static bending and internal bond strength (IB) test were performed on the specimens with the dimensions of 50×200 mm and 50×50 mm, respectively. Modulus of elasticity (MOE), modulus of rupture (MOR) and IB in an air-dry condition were measured according to Japanese Industrial Standard (JIS) A-5908.

Decay and termite tests

Conventional tests were conducted according to JWSA Standard No. 3-1992 and No. 12-1992 for decay and termite, respectively.

2.2.3 Results and Discussion

Weight gain (WG) and antiswelling efficiency (ASE)

WG and ASE of albizzia waferboards due to the both treatments with the cross-linking reagents are shown in Table 2.2.

The values of WGs and ASEs revealed no significant differences above 5 hrs reaction for the formaldehyde treatment : more than 5 hr of reaction caused WG of about 3%, and ASE of more than 60%.

The WGs were increasing with increases of concentrations of solutions on both pad-dry-cure treatments in the range examined. ASE values were not different between the two levels of solution concentrations in both of the reagents.

Thickness swelling (TS) and linear expansion (LE)

The TS and LE of specimens after water soaking at room-temperature and soaking in hot- and boiling-water are shown in Figs. 2.8 and 2.9. The TSs of formaldehyde-treated boards were definitely smaller than untreated boards, and almost the same in any level of the

Table 2.2. WG and ASE of albizzia waferboard treated with cross-linking reagents.

Reagents	Levels	WG(%)	ASE*(%)
(Vapor phase)	React.		
Tetraoxane	5 h	2.9	61.5
Tetraoxane	10 h	3.0	69.7
Tetraoxane	24 h	3.1	71.6
(Pad-dry-cure)	Conc.		
DMDHEU	5%	6.9	76.8
DMDHEU	10%	14.2	74.4
Glutaraldehyde	5%	7.0	71.9
Glutaraldehyde	10%	10.2	74.9

* ASE was measured from the thickness-change of the boards after immersion in water for 3 days.

treatment.

In the pad-dry-cure treatments, TSs of untreated waferboards were about 20%, 25% and 35% after soaking in room-temperature, hot- and boiling-water, respectively. However, when treated with DMDHEU and glutaraldehyde, the swelling after any water soaking conditions were decreased to about 5 to 6%, irrespective of WG. The TSs were not significantly different between the two cross-linking reagents and between the two levels of solution concentrations.

These results indicated that the cross-linking formation by the formalization and pad-dry-cure treatment was stable even after soaking in boiling water for 2 hr, and that these treatments were very effective in reducing the thickness swelling of waferboards.

The LE of waferboards is also very important when they are used for planar materials such as wall and floor. Those of untreated specimens were 0.5, 1 and 1.4% after water soaking in room-temperature, hot- and boiling water soaking. This means that the untreated boards expand in linear direction more than 10 cm per 10 meters in hot-water soaking. These values would cause severe problems if such board materials would be used for flooring or walls. The LEs of chemically-modified boards were less than 0.4% irrespective of water soaking conditions for both formalization and pad-dry-cure treatments.

The TSs of treated boards of the accelerated aging test were remarkably smaller than those of untreated boards during the 4 wet-dry cycles (Fig. 2.10). Repeat soaking of the untreated specimens in water caused more irreversible thickness swelling. However, all treated boards underwent much less thickness swelling through the wet-dry cycles than that of the controls. This should be due to the reduction of hygroscopicity of wood fibers because of the cross-linking formation in hydroxyl groups and/or bulking in the wood cell walls.

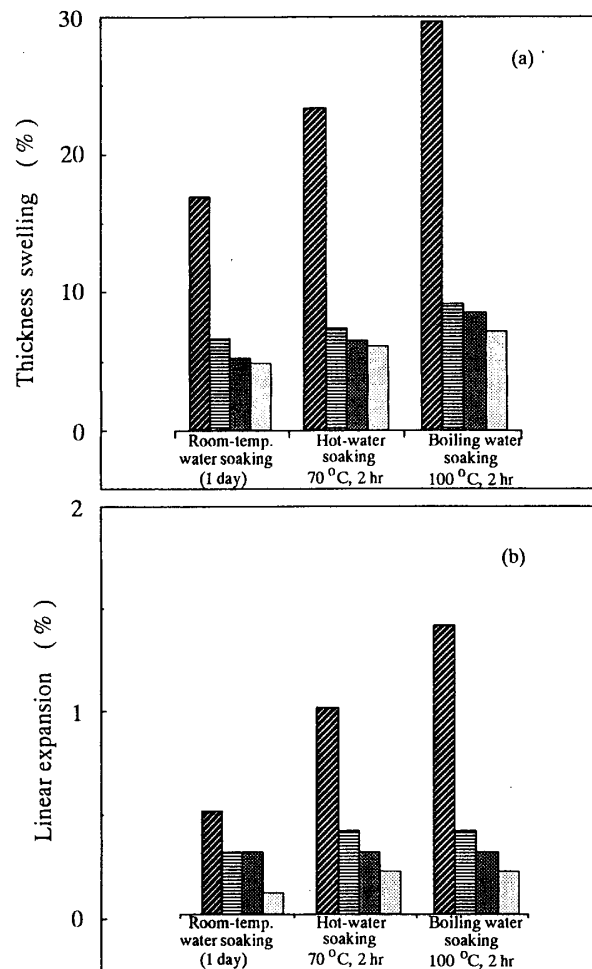


Fig. 2.8. The thickness swelling (a) and linear expansion (b) of waferboards treated with vapor phase formalization at different water soaking conditions. Legend: Control, 2.9% WG, 3.0% WG, and 3.1% WG.

Fig. 2.11 shows the TSs of treated boards when they had been immersed in water for more than three weeks at room temperature. The TSs of the treated boards were smaller than those of the untreated ones in any treatment. The TSs were not significantly different between formalization and pad-dry-cure treatments and between the levels of each treatment.

Mechanical properties

Although the MOR values of treated boards were not different significantly among the reaction times, they were about 40–50% less compared with untreated boards (Table 2.3). This probably was due to the degradation of wood fibers caused by the acid catalyst under the high reaction temperature. Minato⁴⁸⁾ reported that the MOR of solid wood decreased only about 20–30% by the SO₂ catalyzed formalization. On the other hand, they observed

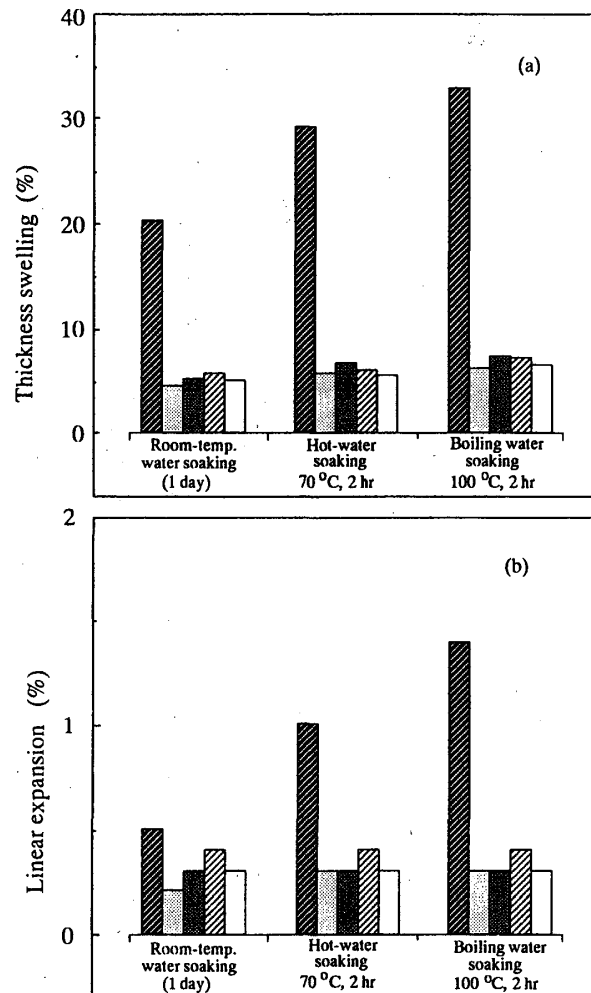


Fig. 2.9. The thickness swelling (a) and linear expansion (b) of waferboards treated with pad-dry-cure treatments at different water soaking conditions.

Legend: : Control, : 5% DMDHEU, : 10% DMDHEU, : 5% glutaraldehyde, and : 10% glutaraldehyde.

a loss of MOR of about 50% for MDF treated under the same reaction condition⁴⁹⁾. The greater decrease of MOR for MDF may have resulted from the degradation of the adhesive resin. Also in this case, the thermal degradation of adhesive resin cannot be neglected. However, the decrease of the substantial ratio of the wood itself in the waferboard should not have caused the considerable reduction of mechanical properties because the WG was not so large as in the case of acetylation.

The MOE values of treated boards increased slightly except at the reaction time of 5 hr. It is usual for the MOE of solid wood and reconstituted wood products to increase to some extent after formalization^{9,50)}. The increase of MOE is thought to partly result partly from the cross-linking formation which restrains the slippage between the fibers and/or fibrils. It

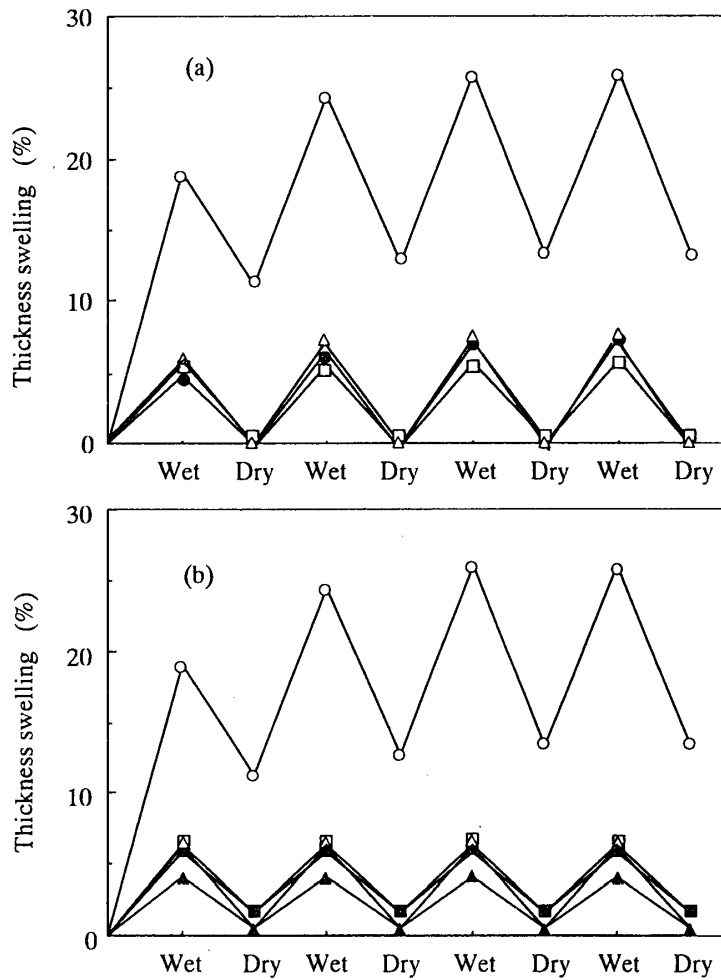


Fig. 2.10. The thickness of the treated and untreated waferboards during accelerated aging test of 4-cycle soak-dry.
 Legend: a: Vapor phase, b: Pad-dry-cure treatment,
 ○: Control, ●: Control, ●: 2.9%, □: 5% DMDHEU, ◻: 3.0%, ■: 10% DMDHEU, △: 3.1%, △: 5% glutaraldehyde, ▲: 10% glutaraldehyde

was known that the MEE of the medium-density fiberboard increased as much as the ASE by the formalization⁴⁷⁾. Therefore, the decrease of equilibrium moisture content by the formalization is another factor increasing the MOE.

The IB strength values of the formaldehyde-treated boards increased with increasing reaction times. Minato⁴⁹⁾ reported a remarkable loss of the IB strength for a urea resin type particleboard after formalization. The antipodal result probably is due to the difference of the adhesive resin used in the board makings. In the case of acetylation, Subiyanto *et al.*⁴⁶⁾ reported that the IB strength of acetylated board decreased considerably with increasing WG by acetylation, due to the substitution of wood hydroxyl in the acetyl

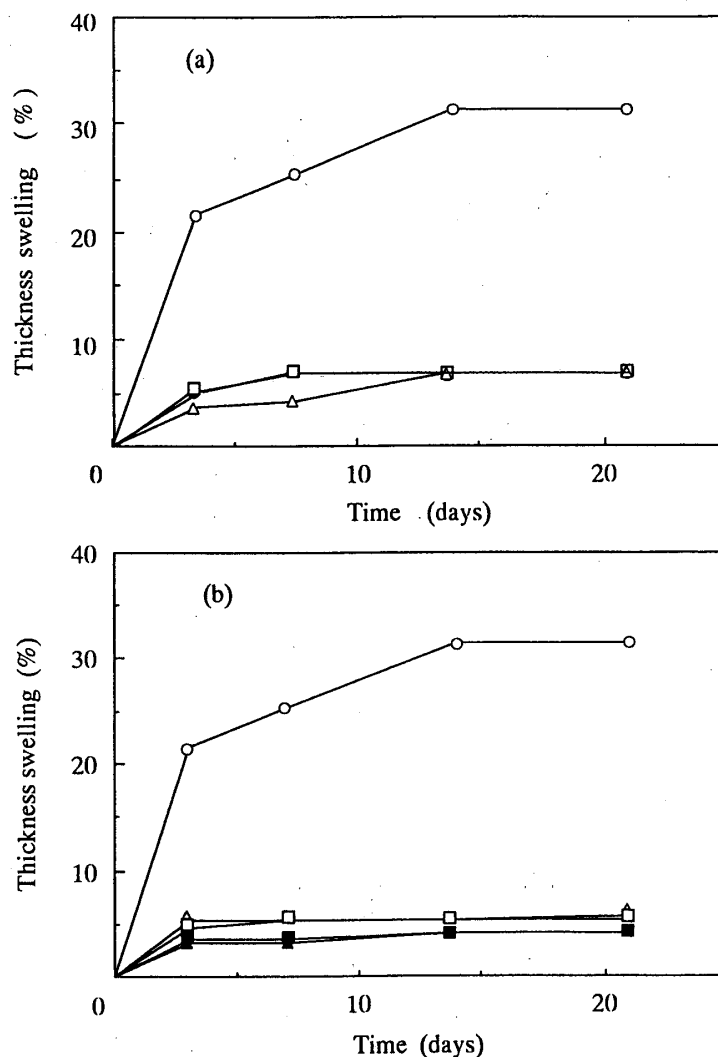


Fig. 2.11. The thickness of the treated and untreated waferboards during water soaking at room temperature.
Legend: See Fig. 2.10.

bond which inhibited the chemical bonding between the wood substance and the resin. Another reason for the small values of the IB strength of acetylated boards was the hydrophobic nature of the substituted units which would cause poor wetting conditions of the wood²²⁾. However, in the case of formalization, because the treatment was conducted after board making, the decrease of the adhesion force should not be of concern. Therefore, if the remaining reactive sites take part in the formalization, the increase of IB strength is not improbable always.

Biological resistance

The WLs of waferboards after 12 weeks exposure to the brown-rot fungus, *T. palustris*, and the white-rot fungus, *C. versicolor*, and after 9 weeks exposure to subterranean termites of *C. formosanus* are presented in Table 2.4.

Table 2.3. IB, MOR and MOE of untreated and treated boards.

Agents	Level	Mechanical properties(kgf/cm ²)		
		IB	MOR	MOE ($\times 10^3$)
	Control	7.0	173.7	23.8
(Vapor phase)	React. time			
Tetraoxane	5 h	3.3	92.8	20.5
Tetraoxane	10 h	4.3	97.6	24.0
Tetraoxane	24 h	5.1	88.2	25.0
(Pad-dry-cure)	Conc.			
DMDHEU	5%	5.9	76.3	21.7
DMDHEU	10%	4.1	76.4	23.8
Glutaraldehyde	5%	7.1	125.5	23.8
Glutaraldehyde	10%	6.3	91.0	23.9

The WLs of untreated boards after exposure to *T. palustris* and *C. versicolor* were 53% and 47%, respectively. However, after the treatments with vapor phase formalization for 5 or more hours, complete elimination of decay was gained.

As described before, adhesive greatly affected growth of fungi in particleboards and fiberboards and isocyanate resins can have a promoting effect, phenolic resins, an impending effect. The large WL of the decayed waferboards in this experiment was assumed to be caused by the non-toxic adhesive used.

Table 2.4. The WL of cross-linking regents-treated boards after biological resistance test.

Agents	Level	Decay test (WL)		Termite ³⁾ test	
		TYP ¹⁾	COV ²⁾	WL(%)	TM(%)
	Control	53.0	46.6	15.5	27
(Vapor phase)	React.time				
Tetraoxane	5 h	-0.3	-0.6	6.1	100
Tetraoxane	10 h	-0.1	-0.5	10.3	100
Tetraoxane	24 h	-0.1	0.7	4.8	100
(Pad-dry-cure)	Conc.				
DMDHEU	5%	4.8	5.8	10.4	100
DMDHEU	10%	3.1	3.5	12.4	100
Glutaraldehyde	5%	15.8	1.7	9.0	100
Glutaraldehyde	10%	4.0	0.4	7.7	100

1) *Tyromyces palustris*. 2) *Coriolus versicolor*. 3) *Coptotermes formosanus*.

In the pad-dry-cure treatments, complete elimination of decay could not be attained as observed in the vapor-phase formalization. However, the DMDHEU-treated boards showed the relatively small WLs in both levels of WGs at about 3 to 6% after the attacks by *T. palustris* and *C. versicolor*. When albizia wafers were treated with glutaraldehyde and processed into boards, the treated boards revealed nearly nil of WL after the attack by *C. versicolor*, but they suffered about 6% and 4% of WLs after the attack by *T. palustris*.

The values of WLs and TM of treated boards after the force-feeding test by termites *C. formosanus* are shown in Table 2.4. The effectiveness of these treatments in resisting termite attack was not as sufficient as was decay resistance. However, 100% TM was achieved by the low level of treatments.

2.3 Hygroscopic Properties and Biological Resistance of Medium-Density Fiberboard (MDF) Treated with Vaporous Formaldehyde

2.3.1 Introduction

Medium-density fiberboard (MDF) is one of the most promising reconstituted wood products from the viewpoint of effective use of wood resources such as small-diameter logs, core of veneer cuttings, and other wood wastes. Moreover, MDF can be widely used as interior materials, furnitures, and a part of audio articles and musical instruments because of its high homogeneity and easy processing. The exhaustion of wood resources will extend the use of MDF to replace plywood in the near future.

One of the most inferior properties of MDF is dimensional instability. MDF consists of small elements that are porous enough to be treated with gaseous chemicals. Vapor phase treatment has a very high possibility to be practically applied to board treatment, especially MDF from the viewpoints of treatability and cost performance.

This chapter is focused on the formalization of MDFs in vapor phase to improve the resistance to fungi, subterranean termites and other biological agents as well as hygroscopic properties.

2.3.2 Materials and Methods

Materials and procedure of formalization

Two kinds of commercial MDFs, made from softwood (S-MDF) and hardwood fibers (H-MDF) bonded with urea-formaldehyde resin, produced by Hokusin Co., Ltd., were used. The thickness of MDFs was about 9 mm and the oven-dried specific gravities were 0.60 and 0.65, respectively. In addition, a special board made from hardwood fibers without adhesive resin was also subjected to the part of decay test. The specimens were cut into 20 mm square.

The vapor phase formalization was conducted at 120°C following the same manner as described in Section 1.1. After treatment, the specimens were heated under vacuum. The WG was calculated from the weight difference before and after treatment.

Measurements of dimensional stability and hygroscopicity

A piece of 50 mm square S-MDF was used for each treatment. In addition to the MDFs treated with formaldehyde for 4 to 24 hr at 120°C, those heated in SO₂ and in air without formaldehyde for 24 hr at 120°C also were subjected to the tests.

The adsorption isotherms were obtained over saturated salt solutions in desiccators at 20°C. At each relative humidity, thickness swelling (TS) and equilibrium moisture content (EMC) were determined. The moisture excluding efficiency (MEE) was defined by

$$\text{MEE (\%)} = \{1 - (\text{EMC of treated} / \text{EMC of untreated})\} \times 100.$$

The ASE values of the specimens subjected to the biodegradation tests were determined separately from the TS in a water-swollen state at room temperature.

Decay and termite tests

Conventional decay and termite tests were employed according to JWSA Standard No. 3-1992 and Standard No. 12-1981, respectively, as has already been described in Section 1.1. In addition the specimens were also subjected to soil burial test for 9 months at 28°C under moist and unsterilized soil enriched with humus.

Bending creep test under progressive fungal attack

The decay chamber consisted of a stainless steel wire-frame with a wire mesh at the bottom. Mycelial fragments of the test fungus from a shake culture were spread aseptically at the bottom tension surface of the test board (50×300 mm wide and 9 mm thickness). A tray containing sterilized water was set at the bottom of the chamber to maintain a humid environment. The chamber was enveloped in a polyethylene bag with a porous plug of silicon rubber to enable fungal respiration. Weight was applied at the center of the boards span from outside the decay chamber (Fig. 2.12). Length of span was 25 cm and loading was fixed at the value which caused 1 mm (1/300 of span) initial deflection. Deflection of

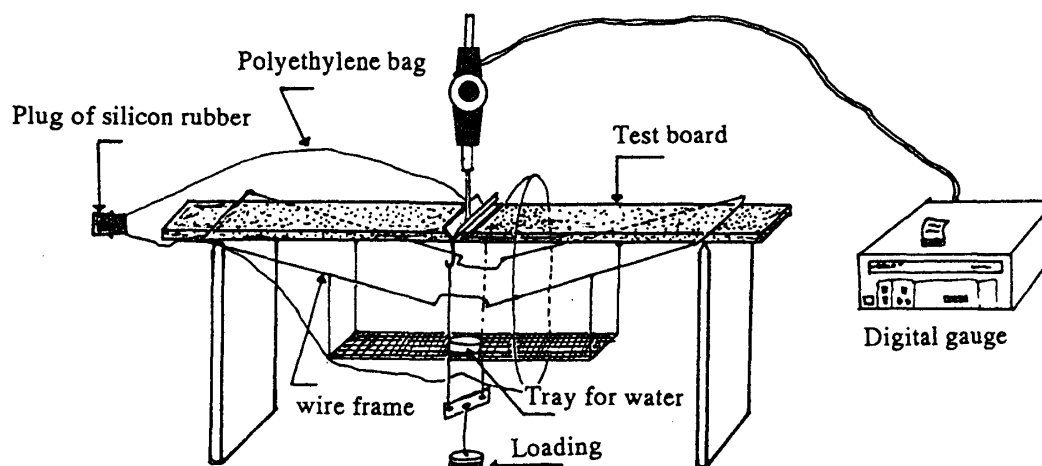


Fig. 2.12. Equipment for bending creep test under fungal attack of *Tyromyces palustris*.

the board at the center of the span was measured continuously at time intervals of one hour with an electric dial-gauge. The chamber was kept in the conditioning room throughout the test period. After 150 days, weight loss of boards was determined.

In this case, only *T. palustris* was used for testing, because the fungus, the brown-rotter generally caused a large strength reduction in reconstituted wood products as well as solid wood.

2.3.3 Results and Discussion

Dimensional stability

The ASE and WG values of the MDFs subjected to the biological deterioration tests are shown in Table 2.5.

The maximum ASE value was obtained from both MDFs treated for 12 hr. High ASE values indicates that oxymethylene linkage occurred between formaldehyde and OH-groups of the wood components, although the fiber was coated by urea-formaldehyde resin during the production of MDF. However, if the reaction time was extended to 24 hr, an adverse effect ASE declined was obtained. This suggests that some degradation due to an excessive reaction occurred in the bonding. This excessive treatment accelerated the degradation of adhesive resin as well as the formation of formaldehyde cross-links, and the former might cause the spring back of compression strain when the MDF was exposed to moisture or water.

The ASEs of formaldehyde-treated S-MDF were higher than those of H-MDF excepting in 2 hr reaction. This indicates that softwood fiber reacts easier with formaldehyde than that of hardwood. However, WGs were not significantly different between both MDFs. Therefore, introduced formaldehyde in H-MDF might be less effective in enhancing ASE than that in S-MDF.

Figure 2.13a shows the dependence of TS on relative humidity. The TS value at 100% R.H., which was determined after water soaking for one day at room temperature, decreased by formalization up to 8 hr, but it rather increased with longer reaction periods. This suggested also by the extremely large TS values at 100% R.H. of MDFs heated only with SO₂ or air, although in the low humidity region these were remarkably less than untreated

Table 2.5. Correlation between antismelling efficiency (ASE) and weight gain (WG) of formaldehyde-treated MDFs.

Run No.	Reaction time (hr)	S-MDF		H-MDF	
		ASE (%)	WG (%)	ASE (%)	WG (%)
1	2	2.3	0.68	4.0	1.19
2	5	49.8	2.67	27.1	2.52
3	12	66.0	4.79	60.5	4.80
4	24	58.8	4.78	46.5	5.29

Note: Mean values of 5 specimens.

MDF. The reason why the TS values of the MDFs heated without formaldehyde became small in the low humidity region probably are attributable to the thermal stabilization of wood based materials, that is, loss of moisture adsorption sites in wood constituents, which generally were known for the heating effects of wood and paper. It can be said that antipodal factor becomes predominant under drastic reaction conditions.

Figure 2.13b shows the EMCs at various relative humidities. The smooth curves in the figure were drawn by applying the adsorption equation proposed by Hailwood and Horrobin⁵¹⁾. While TS increased exponentially (Fig. 2.13a), the EMC showed the well-known sigmoid curve. This inconsistency suggests that all of the adsorbed water molecules always do not contribute to the swelling of MDF. Hailwood and Horrobin⁵¹⁾ classified the adsorbed water into dissolved water and hydrated water, and the latter may correspond to the water which takes in the swelling of MDF.

The EMC of formaldehyde-treated MDF decreased in all humidity ranges, however, excessive treatment rather reduced the degree of reduction in EMC. This reflects the expansion of the moisture accessible surface as a result of the degradation of resin. Even by the heating without formaldehyde, the EMC in the low humidity region became less than that untreated, although it was reversed in the high humidity region because for the same reason stated above.

The ASEs determined under various relative humidity are shown in Fig. 2.14a. The

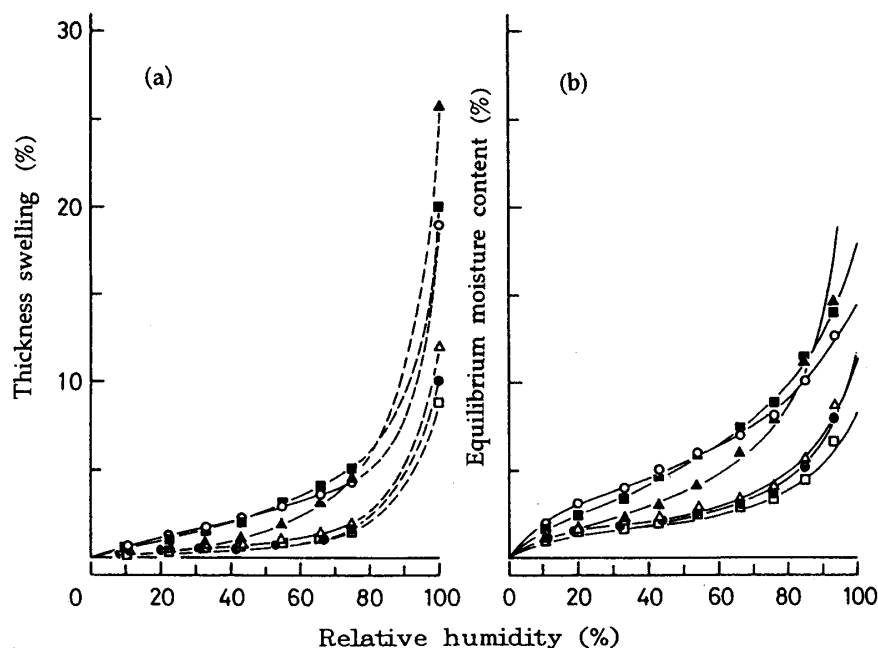


Fig. 2.13. Dependence of thickness swelling (a) and equilibrium moisture content (b) of formaldehyde-treated S-MDF on the relative humidity.

Legend: ○: Control, △: formaldehyde-treated for 4 hr, □: 8 hr, ●: 24 hr, ▲: heated in SO₂ for 24 hr, ■: heated in air for 24 hr.

ASE tends to be estimated high at low relative humidity, especially it went over 90% for the MDF treated for 8 hr. Even by heating without formaldehyde ASE was achieved to some extent, although it became negative in higher relative humidity region.

In Fig. 2.14b, the MEE was plotted against relative humidity. The MDFs treated with formaldehyde were estimated most highly in the vicinity of 50% R.H., whereas those heated without formaldehyde decreased extremely with increases of relative humidity.

Fig. 2.15 shows the swelling of the MDFs after soaking in boiling water for 2 hr. When

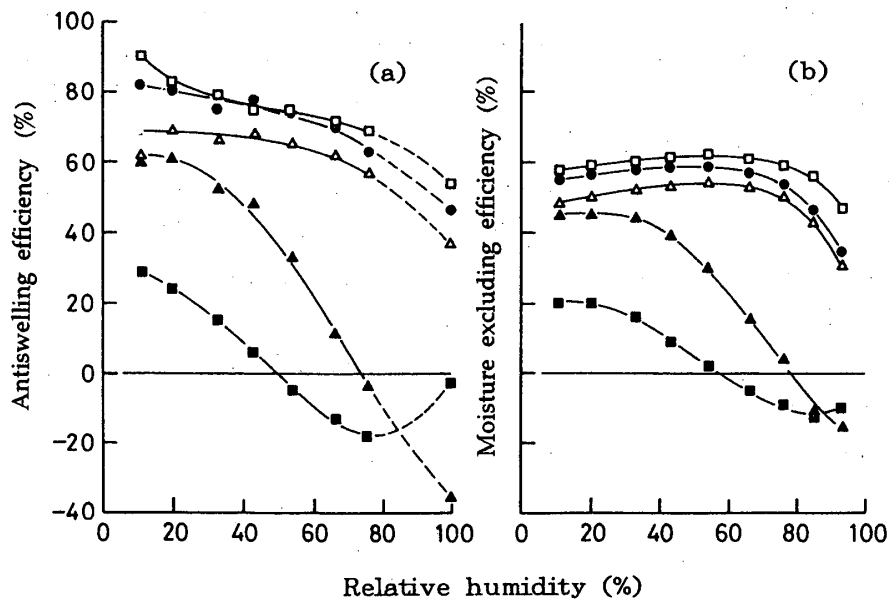


Fig. 2.14. Dependence of antiswelling efficiency (a) and moisture excluding efficiency (b) of formaldehyde-treated S-MDF on the relative humidity. Legend: See Fig. 2.13.

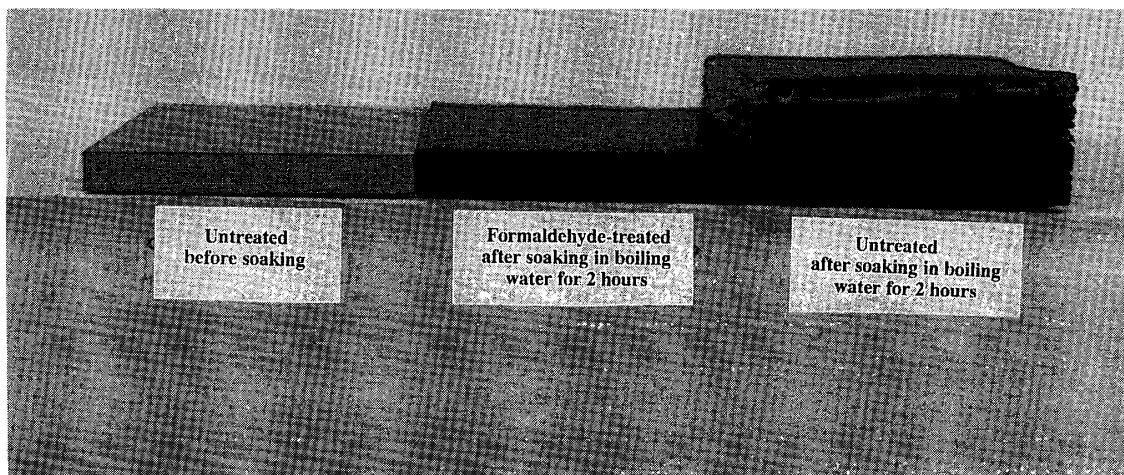


Fig. 2.15. The swelling of the untreated and formaldehyde-treated S-MDFs after soaking at boiling water for 2 hr (Photo: by K. Minato and his courtesy).

boiled, the untreated MDF swelled infinitely to a large extent, whereas treated MDF swelled only about 20%. This value is comparable to the swelling of untreated specimen after soaking in cold water and drying. Formalization of MDF was evidenced very effective to enhance the swelling resistance against severe condition.

Decay resistance

WLs of the both MDFs after decay tests are shown in Table 2.6. They did not reduce satisfactorily but the decay-suppressing effect was highest for *C. versicolor* exposed H-MDF when comparing WL-values between untreated and treated ones.

The WLs of untreated MDFs exposed to *T. palustris* were extraordinary smaller than any other reconstituted wood materials. Similar results were gained when testing H-MDFs glued with other different types of urea formaldehyde and melamine formaldehyde resins (Table 2.7). However, 40% of WL was given in the untreated H-MDF exposed to this fungus when it was processed without resin (Fig. 2.16). This indicates that attack by *T. palustris* was prevented by the resin itself applied to the MDF and that effect of formalization was undetectable for this fungus. However, as shown in Fig. 6.5, the effect was clearly evidenced providing the virtual elimination of decay at the shortest reaction.

As shown in Table 2.6 and Fig. 2.16, decay-suppressing effect rather declined after the longest reaction time, irrespective of the presence of resin. This might be due to the some destruction of cell wall structure and/or some degradation of cell wall components by prolonged heating and action of SO₂-catalyst, which eventually caused the easier penetration of fungal mycelium into MDF.

Table 2.6 The WL in percent of MDF after decay test for 12 weeks.

Reaction time (h)	<i>Tyromyces palustris</i>		<i>Coriolus versicolor</i>		Soil burial	
	H-MDF	S-MDF	H-MDF	S-MDF	H-MDF	S-MDF
Control	3.3	8.0	68.5	18.8	22.0	29.9
2	3.1	6.7	47.9	5.2	23.7	24.3
5	4.4	7.7	8.3	4.3	13.2	11.1
12	5.3	13.5	4.4	7.2	8.8	12.8
24	7.0	11.0	8.1	10.5	11.0	14.1

Note: Average of 9 replicates

Table 2.7. The WL in percent of untreated H-MDF with different resin type after exposure to decay fungi for 12 weeks.

Fungi	H-MDF (Urea)	H-MDF (Melamine)
<i>Tyromyces palustris</i>	0.8	0.9
<i>Coriolus versicolor</i>	33.8	33.8

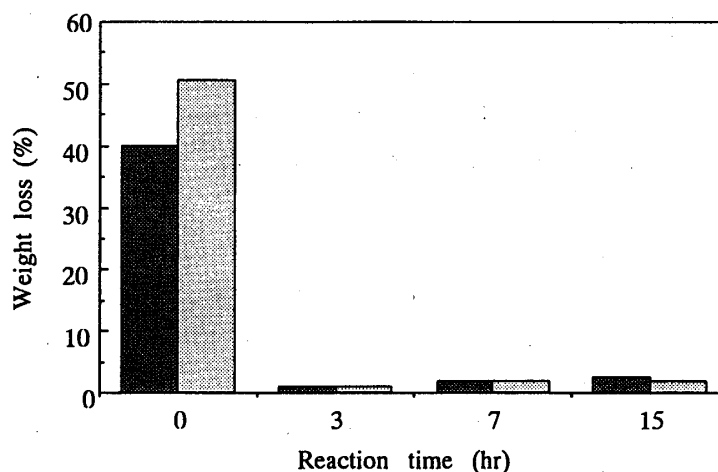


Fig. 2.16. Weight loss of formaldehyde-treated resin resin-free MDF after exposure to decay fungi for 12 weeks.

Legends: ■: *Tyromyces palustris*, □: *Coriolus versicolor*.

The MC of formaldehyde-treated MDF after exposure to *C. versicolor* and *T. palustris* for 12 weeks are shown in Table 2.8. The MC values of treated MDFs were lower than those of untreated ones but were still more than 70%. This might be mainly by a capillarity water absorption from the nutrient medium, and enabled the fungal propagation into MDF. However, fungi could not breakdown of cell wall components easily because of the blocking of hydroxyls by formalization. Higher swelling values of untreated MDF were gained than those of in the formaldehyde-treated MDF (Table 2.9). This indicates that formaldehyde treatment is effective to maintain the dimensional stability even after decay test.

Bending creep test under fungal attack

Both treated and untreated control MDFs were subjected to bending creep test under fungal attack of *T. palustris*. Detection of bending deformation during fungal attack is

Table 2.8. Moisture content (MC) of formaldehyde-treated MDFs after subjected to decay fungi test for 9 weeks.

Reaction time (h)	MC (%)			
	TYP		COV	
	H-MDF	S-MDF	H-MDF	S-MDF
Control	100	140	314	156
2	96	134	225	97
5	85	98	88	83
12	78	97	74	81
24	87	102	86	87

Legend: TYP: *Tyromyces palustris*, COV: *Coriolus versicolor*.

Note: Mean values of 9 specimens.

Table 2.9 Average swelling of formaldehyde-treated MDFs after exposure to *Tyromyces palustris* and *Coriolus versicolor* for 12 weeks, and unsterilized moist soil for 9 months.

Specimens	Reaction time (hr)	Swelling (%)		
		TYP	COV	Soil burial
S-MDF	Control	51.8	28.5	49.9
	2	44.8	14.8	34.1
	5	19.3	7.1	17.1
	12	9.7	2.7	11.0
	24	11.1	4.3	5.0
H-MDF	Control	20.8	14.0	30.1
	2	27.7	22.6	21.7
	5	15.7	1.2	10.2
	12	11.9	4.4	7.4
	24	9.3	5.3	3.3

Legend: TYP: *Tyromyces palustris*, COV: *Coriolus versicolor*.

Note: Mean values of nine specimens.

assumed to be a more reliable way to diagnose the biological resistance of board materials than by using the values of WL, since decay fungi often caused large strength loss at small weight loss.

The resultant deformations of MDFs through bending creep test under fungal attack are shown in Fig. 2.17. Untreated MDFs showed a rapid increases of deflection at the

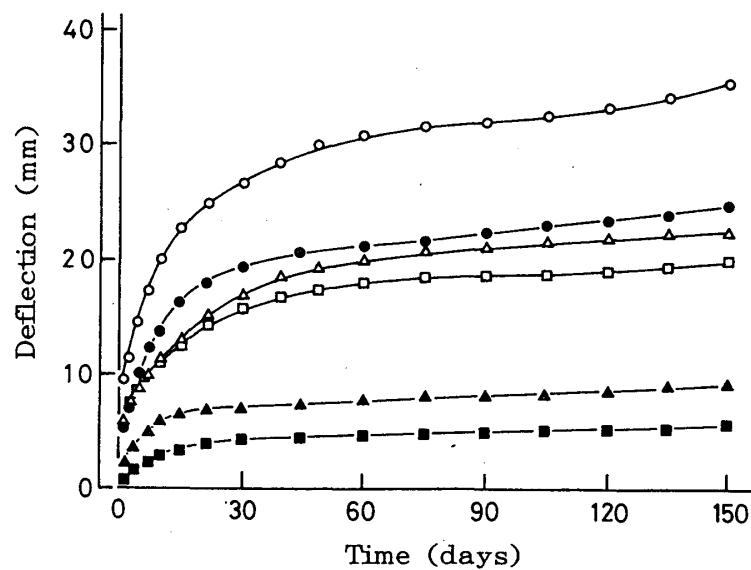


Fig. 2.17. Deflection-time curves of untreated and formaldehyde-treated MDF in bending creep test under progressive attack by *Tyromyces palustris*.

Legend: ASE of softwood MDF ○: 0% (control), △: 31%, □: 42%, ASE of hardwood MDF ●: 0% (control), ▲: 44%, ■: 60%.

beginning of the test and continued to yield large deflection throughout the testing period, while treated MDFs had small deflection even after the long-term loading. As shown in Table 2.10, the formaldehyde treatment did not effectively reduce the WL of MDFs due to the attack by *T. palustris*. Therefore the moisture excluding effect of the treatment may be mainly attributed to the restrain of creep deformation. These low deflection under load will extend the utility of MDF in a humid state with biological hazards.

Table 2.10. Weight loss (WL) of formaldehyde-treated MDFs after 150 days bending creep test under attack by *Tyromyces palustris*.

Specimens	Reaction time (hr)	WG (%)	ASE (%)	WL (%)
S-MDF	Control	—	—	7.9
	3	0.82	31.3	6.3
	6	1.45	42.5	4.7
	24	6.56	48.1	0.7
H-MDF	Control	—	—	2.2
	3	1.31	18.1	1.8
	6	2.72	43.8	1.6
	24	6.83	59.8	0.9

Note: Mean Values of three specimens.

Termite resistance

Table 2.11 shows the WLs of untreated and treated MDFs after forced-feeding tests of termites. When S-MDF was exposed to *C. formosanus*, the WLs decreased with reaction times from about 40% for untreated MDFs to about 10% for treated ones for 24 hr. On the contrary, the WLs of treated H-MDF did not much decrease, although even untreated H-MDF was not attacked as much as in that of S-MDF. The WLs of both MDFs exposed to *R. speratus* also decreased with reaction times.

Table 2.11. Weight loss in percent of formaldehyde-treated MDFs after exposure to *Coptotermes formosanus* for 9 weeks and to *Reticulitermes speratus* for 3 weeks.

Reaction time (h)	S-MDF		H-MDF	
	<i>C. formosanus</i>	<i>R. speratus</i>	<i>C. formosanus</i>	<i>R. speratus</i>
Control	38.1	2.9	9.9	2.1
2	35.5	3.5	7.9	0.6
5	14.8	2.2	6.0	0.6
12	11.7	1.8	4.3	0.3
24	9.1	2.3	4.9	0.3

Note: Mean values of three specimens.

Figure 2.18 shows the mortalities of *C. formosanus* in the same forced-feeding test. Only less than 20% of the *C. formosanus* fed on untreated MDFs died in 9 weeks, whereas all termites fed on treated MDFs were dead within 7 weeks. The fact that about 20% of the *C. formosanus* was dead within nine weeks even when it was fed on untreated solid wood⁵⁰⁾, suggests the harmlessness of untreated MDFs themselves; nevertheless they should include free formaldehyde which was not concerned in the resinification. Therefore, free formaldehyde itself was not toxic, but the ingestion of the reaction products did damage the termites. Furthermore, the slow increases of mortality curves imply that the ingestion of treated MDF did not harm directly the termite, but influence the digestive process and/or absorption of nutrients. For the soldier termites, which generally obtain nutrients from worker termites, the lack of nutrients may have severely affected the digestion process, and were completely dead within 2 weeks.

The mortality of the less aggressive *R. speratus* fed on untreated MDF were also about 30%, whereas those on treated MDFs attained 100% within 3 weeks (Fig. 2.19).

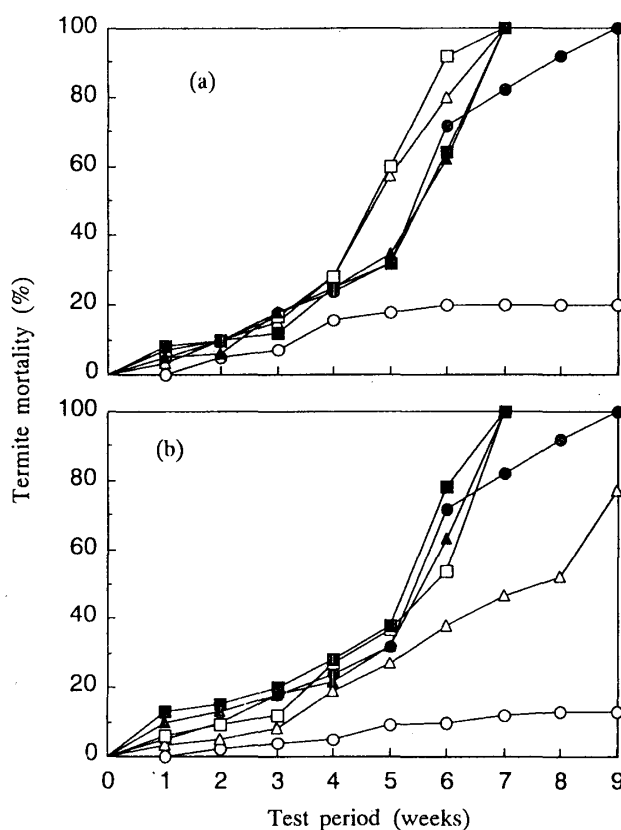


Fig. 2.18. Mortality of worker termite of *Coptotermes formosanus* fed on softwood (a) and hardwood MDFs (b).

Legend: ○: Control, ●: Starvation, formaldehyde-treated for, △: 2 hr, □: 5 hr, ▲: 12 hr, ■: 24 hr.

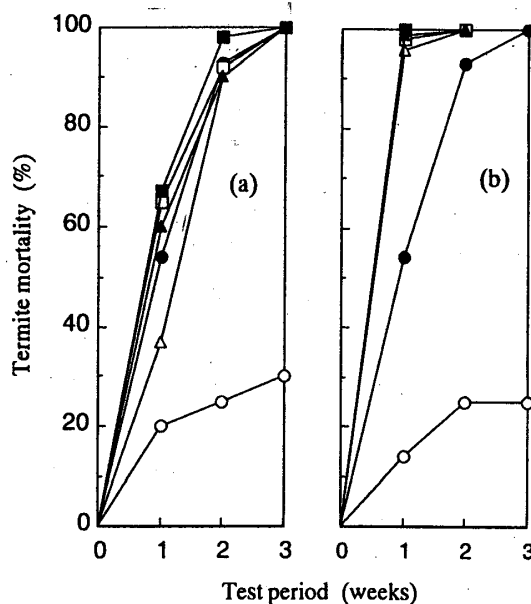


Fig. 2.19. Mortality of worker termite of *Reticulitermes speratus* fed on softwood (a) and hardwood MDFs (b).
Legend: See Fig. 2.18.

Conclusion

In this dissertation, Chapter 1 deals with properties enhancement of solid wood by cross-linking formation and Chapter 2 involves its application to the reconstituted wood products to contribute the efficient and long-term use of forest resource.

By the vapor phase formalization, decay of sugi (*Cryptomeria japonica*) was virtually eliminated at about 5% and 20% levels of resultant antiswelling efficiency (ASE) for brown-rot fungus *Tyromyces palustris* and white-rot fungus *Coriolus versicolor*, respectively in the laboratory test. The treatment was also successful in soil burial test by which the resistance to soil-inhabiting microorganisms was able to access. However, for buna (*Fagus crenata*), the vapor phase treatment was not so effective in resisting to decay, especially to *T. palustris*. The treatment could reduce the attack by subterranean termites. The mortality of destructive *Coptotermes formosanus* reached 100% after 9 weeks and the weight loss by attack declined with increase of reaction time of formalization. These effects were shown more rapidly in less aggressive *Reticulitermes speratus*. These termite resistance seemed to be caused by some metabolic trouble and not by direct toxicity of formaldehyde.

The liquid phase formalization was also evaluated by the same way in this chapter. The treatment was effective in reducing weight loss of sugi exposed to *C. versicolor*, soil fungi and *R. speratus*, and buna exposed to both termites. However, the treatment was ineffective for *T. palustris* and was ranked below than the vapor phase formalization. The liquid phase formalization available at an ambient temperature may be still advantageous in yielding

small strength loss of wood during the process.

In Section 1.2, effect of treatments with other non- or low-formaldehyde cross-linking reagents such as glutaraldehyde, glyoxal and dimethylol dihydroxyethylene urea (DMDHEU) were evaluated. These treatments consist of impregnation of reagent at ambient temperature and heat-cure at 120°C. Therefore, they are not conducted entirely in liquid phase, and called "pad-dry-cure" treatments. Among reagents, glutaraldehyde was ranked best and was superior to formalization in enhancing the resistance of treated wood against decay resistances found in the formalization, particularly in buna exposed to decay fungi, were much improved by the glutaraldehyde treatment.

In Section 1.3, weathering properties of wood treated with cross-linking reagents were investigated. Among the four reagents tested, DMDHEU was ranked best in color stability. All reagents provided better checking resistance than did untreated control but any significant difference was not seen among them. For decay resistance after weathering, formaldehyde had the best performance among these reagents.

Chapter 2 deals with the application of cross-linking formation to the reconstituted wood products such as laminated veneer lumber (LVL), waferboard and medium density fiberboard (MDF).

In Section 2.1, the performance of LVLs, made from the veneers of Douglas fir (*Pseudotsuga menziesii*), was evaluated. Vapor phase formalization and pad-dry-cure treatment with glutaraldehyde and DMDHEU were applied to the veneer prior to the LVL production. Decay was virtually eliminated in all treated LVLs at relatively low levels of treatment. All treatments could reduce the weight loss caused by termite attack, but the resistance was not as sufficient as was decay resistance. All treated LVLs were very stable to water soaking even in the 2-hour boiling for thickness swelling as well as linear expansion along tangential direction.

Wafers of fast-growing hardwood of albizzia (*Paraserienthes falcata*) were subjected to vapor phase formalization and pad-dry-cure treatment with glutaraldehyde and DMDHEU, prior to the production of low-density waferboard. All at the treated boards were very stable to soaking in boiling water for thickness swelling and linear expansion. Laboratory test revealed that decay was completely suppressed in formaldehyde-treated boards, low weight loss was gained in other treated boards. All treated boards were also effective in resisting to the attack by destructive termite *C. formosanus*.

Finally in Section 2.3, vapor phase formalization was applied to softwood and hardwood MDFs and their properties were evaluated. The thickness swelling and equilibrium moisture content of treated MDFs decreased in the entire humidity range. The antishwelling efficiency and moisture excluding efficiency of the treated MDFs increased with decrease of relative humidity. Formalized MDFs resisted to decay, particularly without adhesive resin. The treatment could not provide the successful reduction of weight loss by

termite attack, but caused the complete death of termites in forced-feeding test.

In any treatment with cross-linking reagents, introduction of catalyst is necessary to gain the sufficient reaction between wood components and reagent. The conventional formalization method is catalyzed by hydrogen chloride or various metallic chlorides, and it often causes a severe loss of mechanical strength in the treated materials. In the present study, sulfur dioxide, which has been utilized for the cotton fabrics, was adopted as catalyst in all treatments to reduce the strength loss of treated specimens. Effect of these treatments on mechanical properties was investigated only on the formalized albizzia waferboards. The treatment caused a 50% reduction of modulus of rupture but it did not affect the modulus of elasticity, and gave a significant increase of internal bond strength. Vapor phase formalization also provided the decrease of deflection under loading and fungal attack. This was considered mainly to be derived from the moisture excluding effect by the treatment. Among the treatments investigated here, vapor phase formalization seemed better totally than pad-dry-cure treatment. However, some chemicals from the latter treatment was superior to formalization in biological resistance. Although the effect of treatments with cross-linking reagents on physical properties should be investigated in more detail, present results should promise the production of the high-performance wood materials for building and other uses having great biological resistance and improved physical properties.

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